Synthesis of Polycrystalline Spherical SnO_2 Microparticles via Hydrothermal Treatment in the Presence of Mixed Surfactants

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The spherical microparticles of SnO_2 were synthesized successfully by hydrothermal treatment of their precursor consisting of $SnCl_4$ and mixed surfactants, followed by calcination at 500 °C.

Tin dioxide (SnO_2) is a well-known functional material used for gas sensors,[1] dye-sensitized solar cells,[2] and transparent conducting electrodes.[3] Recently, synthesis of SnO_2 nanostructures such as nanorods,[4,5] nanoribbons,[6,7] nanoflowers,[8] and nanowires,[9,10] have been intensively studied for expecting their special electrical and optical properties. It has been well known that the performance of SnO_2-based device, e.g., gas sensors, is strongly affected by various factors such as crystallite size, specific surface area, morphology and surface properties. Thus, the preparation of mesoporous SnO_2 and its thermal stability have also been intensively investigated.[11–13] Some SnO_2 nanostructures showed interesting properties for gas sensors,[7,9,10,14] however, for a gas sensor application, morphological control of SnO_2 is important not only in physicochemical properties but also in gas diffusion properties. As revealed by diffusion equation-based study, the control in size and shape of secondary particles in micrometer scale as well as that of their porosity is also important from a view point of gas penetration depth into a secondary particle of SnO_2.[15,16] On the other hand, recently, Kijima et al. reported that SnO_2 microwires can be synthesized from mixed surfactant nematic liquid crystalline phase.[17] This motivated us to examine the size and shape control of SnO_2 in micrometer scale in the presence of mixed surfactants. In this letter, we report a novel method for the synthesis of microsize spherical SnO_2 particle via hydrothermal treatment in the presence of or absence of surfactants.

All chemical reagents were analytical grade and used without further purification. The typical synthesis method is as follows. Tin chloride pentahydrate ($SnCl_4 \cdot 5H_2O$), nonaethyleneglycol mono-*n*-dodecylether ($C_{12}EO_9$), polyoxyethylene (20) sorbitan monostearate (Tween 60), and H_2O were mixed at a 1:1:1:60 molar ratio at 60 °C. The mixture (total weight of 5.46 g) was transferred into a Teflon-lined stainless steal autoclave (50 mL in volume), and hydrothermally treated at 90–180 °C for 12 h. The obtained precursors were calcined at 500 °C for 3 h in a capped alumina crucible. A similar but surfactant-free reaction was carried out under a selected condition.

In the typical reaction, the starting mixture containing $SnCl_4$ and mixed surfactants was hydrothermally treated at 120 °C for 12 h. The resulting mixtures of highly viscous solution and gel were further calcined at 500 °C for 3 h. It was found that the precursor obtained by hydrothermal treatment of the mixture containing $SnCl_4$ and double surfactants was difficult to evaluate the state, because the precursor was gelation state. The two-step reaction was found to produce uniform spherical SnO_2 microparticles at high yields, as shown in Figure 1a. A similar reaction without surfactants led to spherical microparticles but with a rough surface at low yields (Figure 1b). Similar but smaller SnO_2 microspheres were prepared by the hydrolysis of SnF_2 at 60 °C, along with or without additional hydrothermal treatment.[12] In marked contrast to those obtained in these surfactant-free systems, the microparticles prepared in the surfactant-based system are characterized by their high degree of sphericity as well as their remarkably smooth surface. To our knowledge, this is the first report on the identification of the spherical forms of SnO_2 after calcinations at elevated temperature (500 °C). The marked difference in surface roughness between the microspheres in both systems with or without surfactant makes us to expect that there may be a difference in specific surface area and pore size distribution. Contrary to our expectation, only a little difference in specific surface area was observed for both systems according to preliminary results (28 and 24 m^2/g for Figures 1a and 1b, respectively). This would be due to incomplete separation of microspheres from each other. In order to elucidate the optimal condition for the preparation of microsheres in the presence of surfactants, the effect of hydrothermal temperature was examined. Apparently, as shown in Figure 2, the SnO_2 particles thus obtained were morphologically different in size and shape, depending on the hydrothermal treatment temperature. Especially, the product obtained via hydrothermal treatment at 120 °C was regular spherical shape ranging from 1 to 3 μm in diameter. SnO_2 microshperes were partly formed for the hydrothermal treatment at 150 °C (Figure 2c). In contrast, no spherical particles were obtained for the hydrothermal treatment at as low as 90 °C and as high as 180 °C in spite of the same calcination temperature. These facts indicate that hydrothermal temperature is an essential factor to form microspheres. It is found that, upon prolonging the hydrothermal treatment time gradually up to 12 h, submicro and micrograins were aggregated to form spherical microparticles. However, a 24 h treatment re-

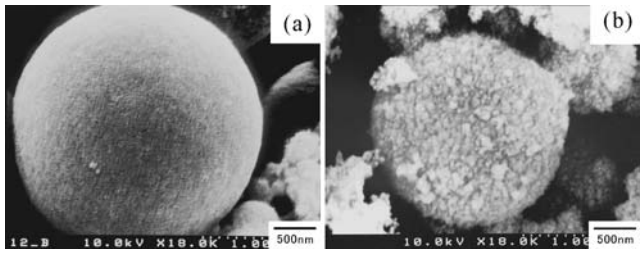

Figure 1. SEM photographs of final products (calcined at 500 °C for 3 h) derived from hydrothermally treated precursors in the presence of surfactants (a) and in the absence of surfactants (b).

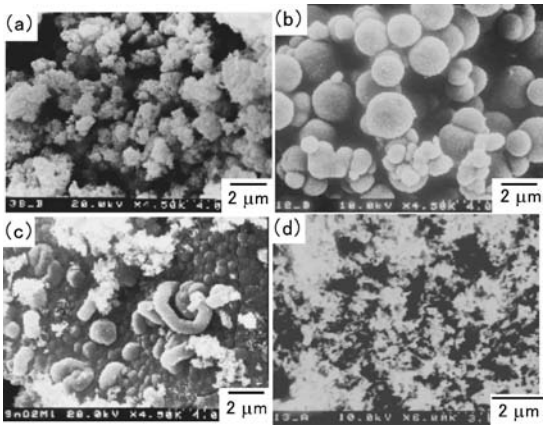

Figure 2. SEM photographs of final products calcined at 500 °C for 3 h. Each products were derived from hydrothermally treated at (a) 90 °C, (b) 120 °C, (c) 150 °C, and (d) 180 °C for 12 h, respectively.

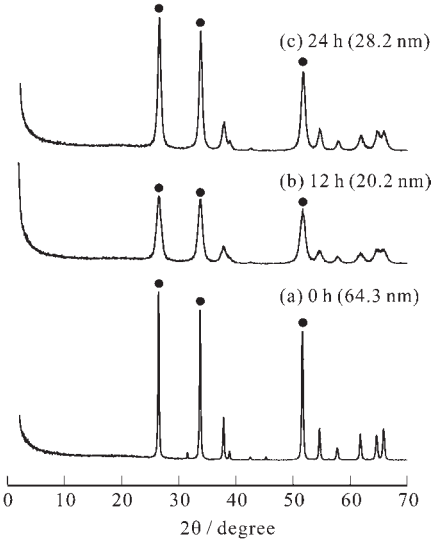

Figure 3. XRD patterns for the final products derived from hydrothermally treated precursors at 120 °C for 0, 12, and 24 h.

sulted in coagulation of small particles. This result implies not only the temperature of hydrothermal treatment but also the treatment time is an important factor to produce such spherical particles. The final products obtained using different times of hydrothermal treatment can be structurally characterized by the XRD patterns shown in Figure 3. All the diffraction peaks for these final products were assigned to those of tetragonal SnO_2 (PDF No. 41-1445), indicating that the obtained microspheres consist of pure SnO_2 phase. EDX measurements revealed that there are no impurities in the final products, although very small amount of chlorine (0.5 wt %) was detected for a few samples. For practical application in gas sensors, the remaining chlorine species will be a serious problem especially for coexisting water vapor. The remaining of chlorine is due to the starting mixtures of $SnCl_4$ and mixed surfactants. However, no impurities could be detected upon washing of the final product with distilled water. This suggests that chlorine species (maybe chlorides) remain on the surface of spherical particles with a weak interaction, and thus it can be easily removed by washing process. The crystallite sizes of the final products were calculated using Scherrer's formula from a large full-width at half maximum of highest XRD peak of SnO_2(110) (Figure 3). As shown in Figure 3a, the product without hydrothermal treatment was large in crystallite size (about 65 nm), and consisted of randomly coagulated particles. In contrast, upon hydrothermal treatment, the product showed a tendency to form spherical particles with relatively small crystallite size (about 20 nm), as shown in Figure 3b. In addition, prolonging the hydrothermal treatment time up to 24 h increased crystallite size slightly and resulted in disappearance of microspheres.

In summary, the present study demonstrates a novel method for the synthesis of spherical SnO_2 microparticles based on a combined use of hydrothermal treatment and calcination. The formation of spherical microparticles depends not only on hydrothermal treatment temperature but also on hydrothermal treatment time. Perfectly spherical particles of SnO_2 are obtained upon calcination at elevated temperature (500 °C). Similar spherical microparticles can be synthesized in the absence of surfactants, but their surface is fairly rough in contrast to those synthesized in the presence of surfactants. Further study is needed to elucidate the formation mechanism of spherical SnO_2 microparticles. In addition, the control of porosity and specific surface area of spherical SnO_2 particles should be investigated for their potential applications. Thus, the applicability of these microspheres to gas sensors is under investigation.

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