

Preparation of Porous SnO₂ Particles Having High Specific Surface Area and High Thermal Stability via an Aqueous Solution Route and Subsequent Hydrothermal Treatment

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Hierarchically tailored SnO₂ particles with a diameter of 200–500 nm were spontaneously formed in aqueous solutions dissolving SnF₂ at 60 °C. The porous architecture of the particles was composed of SnO₂ crystallites of ca. 5 nm in diameter and exhibited a high specific surface area of 130–230 m²/g. Subsequent hydrothermal treatment at 150 °C improved the thermal stability of the SnO₂ fine structure.

Semiconducting SnO₂, which has a wide band gap (≈ 3.8 eV), is widely applied for various devices, such as transparent electrodes, gas sensors, photosensors, photocatalysts, antistatic coatings, and dye-sensitized solar cells, because of its excellent optical and electrical properties and chemical stability. The performance of these devices is greatly affected by the particle size, specific surface area, and surface condition of the semiconducting oxides. Thus, the control of the microstructure is practically important for various applications of SnO₂ and SnO₂-based ceramics. Nanoscale SnO₂ particles have been prepared using spray-pyrolysis,^{1,2} laser ablation,^{3,4} and hydrothermal synthesis.^{5,6} Mesoporous SnO₂ powder was produced by utilizing the self-assembly of surfactants.^{7,8} However, the morphological control in nanoscale was insufficient for a wide variety of applications.

In recent years, aqueous solution routes mimicking the synthesis of inorganic materials in life have attracted great attention because functional inorganic materials are successfully prepared at ambient temperature and pressure.⁹ It was reported that crystalline SnO₂ films were directly grown in solutions dissolving tin(II) fluoride (SnF₂) and chloride (SnCl₂) at a low temperature.^{10,11} Heterogeneous nucleation and crystal growth on a glass substrate were achieved by moderate precipitation through oxidation of Sn(II) in the solutions. The biomimetic approach also provides morphological control of the inorganic crystals with co-existing species. In the present work, we found that porous SnO₂ particles consisting of nanoscale subunits were spontaneously prepared through homogeneous nucleation in the aqueous system. The presence of fluorine mediated the formation of the hierarchical architecture which is applicable as a new type of electrodes and sensors.

A certain amount of SnF₂ (Kanto Chemical) was dissolved in purified water. After stirring for 1 h at room temperature, the solutions were adjusted to be in the range of 0.01–0.25 mol/dm³ of tin concentration and pH 3.1 or 3.2 by addition of 0.1 M HCl or NH₄OH aqueous solutions. Precipitation in the precursor solutions was induced within several hours at 60 °C. White powder separated from the solutions through centrifugation and decantation was washed with purified water and then dried in air at 60 °C for 24 h. Subsequent hydrothermal treatment of the powder was performed in purified water at 100–200 °C us-

ing a Teflon-lined stainless steel autoclave before drying.

Submicrometer-sized particles were slowly precipitated in the precursor solutions. As shown in Figure 1a, spherical particles of 200–300 nm in diameter were obtained with deposition for 24 h in a 0.01 mol/dm³ SnF₂ solution at pH 3.1 and 3.2. Figure 1b indicates that the spherical particles had a hierarchical structure consisting of small subgrains with a diameter of ca. 10 nm. The particle size gradually increased with the deposition time. The macroscopic morphology of the particles depended on the SnF₂ concentration. Ragged particles of 200–500 nm in diameter were produced in 0.05–0.2 mol/dm³ SnF₂ solutions at pH 3.1 and 0.05–0.1 mol/dm³ solutions at pH 3.2. Prickly morphology was observed in a 0.25 mol/dm³ SnF₂ solution at pH 3.1 and a 0.15 mol/dm³ solution at pH 3.2. The particles as grown in the solutions were identified to be crystalline SnO₂ having a rutile structure by X-ray diffractometry (XRD; Rigaku RAD-C) using Cu K α radiation. Lattice image (Figure 2) also showed the presence of nanoscale SnO₂ crystallites (ca. 5 nm) in the particles. The specific surface area and pore-size distribution were calculated by the BET and BJH methods, respectively, based on N₂ adsorption and desorption isotherms at 77 K with a Micromeritics TriStar 3000. As listed in Table 1, the particles exhibited a high specific surface of 130–230 m²/g. The nanoscale grain

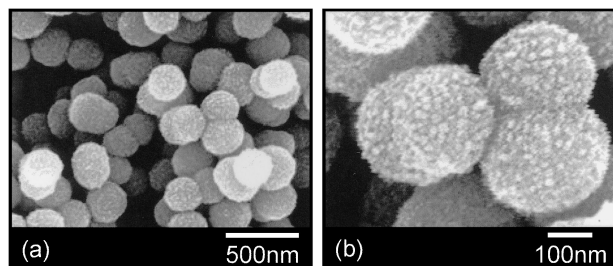


Figure 1. Scanning electron micrographs observed using a Hitachi S-4700 for particles prepared at pH 3.2 and 0.01 mol/dm³ of SnF₂ concentration.

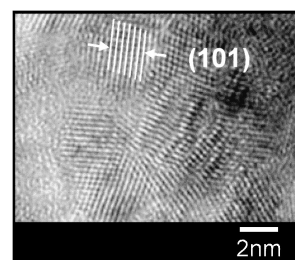


Figure 2. Lattice image observed using a Philips TECNAI F20 transmission electron microscope for particles prepared at pH 3.2 and 0.01 mol/dm³ of SnF₂ concentration.

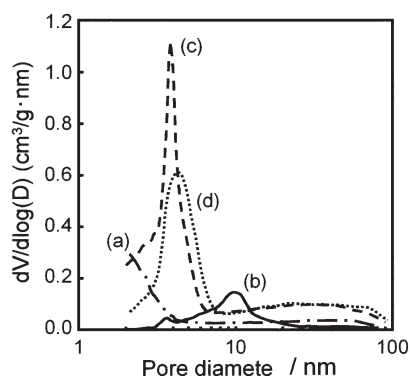
Table 1. Specific surface area (m^2/g) of particles prepared at various conditions

	SnF_2 Concentration/ mol dm^{-3}				
	0.01	0.05	0.10	0.15	0.20
pH 3.1	—	130	173	225	207
pH 3.2	126	136	185	175	—

size was supported by a calculation from a high specific surface area and a large full-width at half-maximum of XRD peaks using Scherrer's formula. Because the distribution of pore size shows the presence of micropores below 3 nm (Figure 3a), the spherical particles had a microporous structure with SnO_2 nanograins.

Crystalline SnO_2 is produced by moderate reactions involving the oxidation of Sn(II) into Sn(IV). The yield of the SnO_2 particles was only 2–3% in the case of a $0.1 \text{ mol}/\text{dm}^3$ SnF_2 solution, and the solubility in water is $0.0014 \text{ mol}/\text{dm}^3$ (at 20°C). This suggests that oxidation reaction was mainly caused by oxygen molecules dissolved in the precursor solution. The moderate reaction rate including the oxidation of Sn(II) is essential for the preparation of crystalline SnO_2 with suppression of the rapid precipitation of amorphous hydroxide. According to the results of X-ray photoelectron spectroscopy (XPS) using a JEOL JPS-9000MC with Mg radiation, ca. 10 mol% fluorine originating from the raw material remained in the precipitates. The absence of the peak shift in the XRD patterns implies that fluorine atoms existed on the surface of the SnO_2 grains. Thus, the formation of a hierarchical architecture containing nanograins is ascribed to the restriction of regular crystal growth with the presence of fluorine on the surface.

Generally, a decrease in specific surface area of SnO_2 at a high temperature is a serious problem for sensing devices. As shown in Table 2 and Figure 3b, the specific surface area considerably decreased and the micropores collapsed with heating at 500°C for 3 h. Thus, the thermal stability of the hierarchical particles was insufficient for practical usages at a high temperature. We found that hydrothermal treatment at 150°C for 72 h significantly increased the specific surface area of the particles with removal of fluorine atoms. Moreover, the specific surface area of the treated particles was maintained above $150 \text{ m}^2/\text{g}$ after heating at 500°C (Table 2). It was reported that hydrothermal treat-

**Figure 3.** Pore-size distribution for particles prepared at pH 3.2 and $0.1 \text{ mol}/\text{dm}^3$ of SnF_2 concentration, (a) as-prepared, (b) with calcination at 500°C , (c) with hydrothermal treatment at 150°C , and (d) with calcination after hydrothermal treatment.**Table 2.** Change in specific surface area (m^2/g) by calcination at 500°C for 3 h and/or hydrothermal treatment at 150°C for 72 h. The original particles were prepared at pH 3.2 and $0.1 \text{ mol}/\text{dm}^3$ of SnF_2 concentration

	Calcination	
	Before	After
As-prepared	185	23
Hydrothermal-treated	243	151

ment suppressed the grain growth of SnO_2 particles at a high temperature.¹² However, the essence of the high thermal stability was not clarified. Here, an increase in the specific surface area and enlargement of pores (Figure 3c) show a shrinkage of SnO_2 nanograins with the hydrothermal treatment. On the other hand, the XRD peak intensity increased with the treatment. These results suggest that the high thermal stability is ascribed to the improvement of the crystallinity of SnO_2 nanograins via rearrangement of the disordered region with removal of fluorine. The effect of the hydrothermal condition was insufficient at 100°C . The neckgrowth between nanograins would occur at 200°C because the surface area obviously decreased with the hydrothermal treatment.

In conclusion, hierarchical SnO_2 particles with high specific surface area and sufficient thermal stability were prepared by crystal growth in an aqueous system containing SnF_2 and subsequent hydrothermal treatment. This new type of porous SnO_2 particles would be useful for various applications as an easy-to-handle form having a high performance and a high durability.

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