

Synthesis of SnO₂ Nanoparticles by the Sol-gel Method From Granulated Tin

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SnO₂ sols were prepared by the sol-gel method starting from granulated tin. Calcining the dried gel powder at 773 K for 2 h formed almost monodispersed SnO₂ nanoparticles whose average diameter was 5 nm and surface area as high as 143 m²/g.

Tin oxide (SnO₂), cassiterite structure, is a typical wide band gap n-type semiconductor (3.8 eV)¹ and one of the most widely used semiconductor oxides because of its interesting properties and applications. It can be used such as transparent electrodes for solar cells, liquid crystal displays, catalysts for methanol conversion, antistatic coatings and gas sensors.¹⁻⁷ Among them, the most important use is for gas sensors. The sensing properties of SnO₂ sensors (sensitivity, selectivity and reproducibility) depend on several factors, mainly crystallite size and specific surface area. For example, the sensitivity begins to increase sharply as crystallite size (*D*) decreases below a critical value (6 nm), which is equal to twice the thickness of the Schottky barrier penetrating into the tin oxide grains, the whole crystallite is depleted of electrons and as a result, the sensitivity of the element to a reducing gas would change with *D*. Reactions between oxygen species and reducing gases to be detected can be improved by increasing the sensing surface area. Consequently, the use of nanoparticles will allow obtaining better responses of these solid state gas sensors.^{3,5}

Tin oxide nanoparticles have been prepared by many different wet chemical methods such as hydrothermal,³ sol-gel,^{1,2,6,7} gel-combustion,⁴ spray pyrolysis methods,⁸ and polymerized complex (PC) method.⁹ Most of the starting materials in sol-gel method are tin chlorides (SnCl₄ or SnCl₂),^{6,7,9} which are generally preferred because they are easy to perform and the cost is lower compared with starting from metal alkoxides M(OR)_{*n*},² but the contamination of chlorine ions cannot be avoided, which affects the surface and electrical properties.⁴ Some samples by hydrothermal method are also made from SnCl₄.³ The gel-combustion method needs a large amount of organics and evolves large volume of gases such as NO_x and CO₂ during the combustion reaction.⁴ In this study, we present a novel sol-gel method for the preparation of SnO₂ nanoparticles starting from granulated tin.

The SnO₂ nanoparticles were prepared as follows: 8 mol L⁻¹ HNO₃ was added to 3 g of granulated tin and 10 g of citric acid contained in a flask until a clear solution was obtained. Aqueous ammonia (25%) was added dropwise to the solution with stirring until a pH value of 8 was reached. The obtained solution was refluxed at 373 K for 2 h. During the refluxing the solution slowly turned into a turbid colloidal solution. After cooling down the Sn(OH)₄ sol was collected from the solution by centrifugation and washed several times with water and ethanol. After drying at 373 K for 5 h, in air, the

gel powder was ground in a mortar, and finally calcined in a muffle furnace at 573, 673, 773 K for 2 h. The structure of the powder was characterized by X-ray diffraction (XRD) (Cu Kα 40 kV, 60 mA, Rigaku D/max 2550v diffractometer). The BET surface areas of the calcined samples were measured with a Micromeritics ASAP 2010 micropore analysis system. The particle shape was observed by TEM (Model 2010CX, JEOL, Peabody, MA).

Figure 1 shows the XRD patterns of the powders obtained at different temperatures, the peak positions in each sample agree well with the reflections of bulk SnO₂ (cassiterite). The width of the reflections is considerably broadened, indicating a small crystalline domain size, which can be roughly quantified using the Scherrer's equation and the half width of the diffraction peak of the SnO₂ (110) plane. The crystallite size of SnO₂ prepared by calcining at 573 K is 3 nm. As the calcining temperature turns higher, the larger sizes of SnO₂ nano particles are obtained, the crystallite sizes are about 4 and 5 nm when calcined at 673 and 773 K, which is due to grain growth of the SnO₂ particles. In other words, the calcining temperature is critical in controlling the particle size. The size of the SnO₂ nanoparticle is smaller than the SnO₂ synthesized by the PC method.⁹ BET specific areas of the samples are listed in Table 1. The much high surface area of the calcined powder may be due to the avoiding of Cl⁻ ions which causes agglomeration between particles.¹⁰ The average particle size (*d*) is calculated by the formula: $d = 6/\rho A$ where ρ is the theoretical density of the material and *A* is the specific surface area of the powder. The results calculated are also listed in Table 1. The particle size calculated from BET surface area coincides well with those from the broadening of XRD peak at lower temperatures. As for the samples calcined at higher temperature, such as 773 K, the particle size is larger than the crystallite size, indicating a low degree of agglomeration.

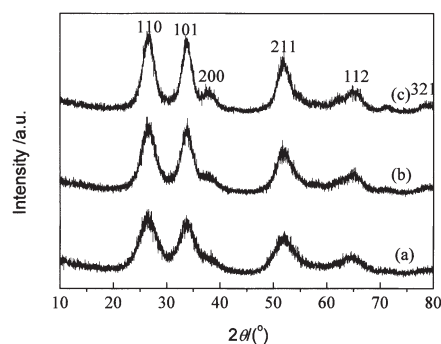


Figure 1. X-ray diffraction patterns of the powders prepared by the sol-gel method with the citric acid as complexing agent. The calcination temperature: (a) 573 K, (b) 673 K, and (c) 773 K.

Table 1. BET specific surface area, average particle and crystallite sizes of the SnO₂ powders prepared from granulated tin

Calcining temp./K	BET surface area ^a /m ² /g	Particle size ^a /nm	Crystallite size ^a /nm	BET surface area ^b /m ² /g	Particle size ^b /nm	Crystallite size ^b /nm
573	289.1	2.9	2.8	161.1	5.3	5.1
673	209.9	4.1	4.0	75.0	11.4	8.4
773	143.1	6	5.1	32.2	26.6	15.2

^aPowders prepared by the sol-gel method. ^bPowders prepared by the direct precipitation method.

It is known that the sol-gel method is a versatile solution technique used to obtain ultrafine, homogenous powders of a variety of glass and ceramic materials at low temperatures and in short times through the growth of metal oxo-polymers in a solvent.^{2,8} The chemistry involved in the sol-gel process is based on the inorganic polymerization of molecular precursors. The sol-gel process involves hydrolysis and condensation, which are generally fast and need to be inhibited to avoid precipitation and allow sol or gel formation. Control of these two steps is of great importance, such control can be achieved by the use of strong complexing ligands, such as citric acid. Citric acid (H₃L) is a weak triprotic acid. Denoting the complex by its general formula M(OOR)_n, where M is the metal ion, sol-gel process may be described as follows.^{11,12}

Hydrolysis,



Condensation,



In this presentation, granulated tin was dissolved when HNO₃ was added and yielded a transparent solution. As previously pointed out,⁸ the chelating ability of citric acid and the complexation reaction between metal ions and citric acid depend highly upon the solution pH. Citric acid dissociated in a step-wise manner in solution, only when pH of the solution was above 6.4, the species L becomes the dominant one. The complexation reaction does not occur in a very strong acid atmosphere. So the pH of the solution in this reaction was adjusted to about 8, the complexation reaction took place and the solution changed into sol slowly when refluxed at 373 K.

By comparison, the SnO₂ nanoparticles were also prepared by the direct precipitation without citric acid as complexing agents. Precipitate was obtained as soon as aqueous ammonia (25%) was added into the solution. The BET specific surface area, average particle and crystallite sizes of the powders calcined at different temperatures are also listed in Table 1. The data indicate that larger particles are obtained by this method and the powder calcinated at higher temperatures shows a high degree of agglomeration.

Figure 2 shows the TEM images of SnO₂ particles prepared by the sol-gel method. Shown in Figure 2a is the SnO₂ particles calcined at 573 K for 2 h. The sizes of the particles fall within the range of 2 nm to 3 nm. The residual C element of the citric acid which had not been combusted yet is shown in the EDS. The inserted electron patterns appear to be typical polycrystalline diffraction rings. According to the diameters of the rings, the spacings are 0.33, 0.27, and 0.18 nm, respectively. They

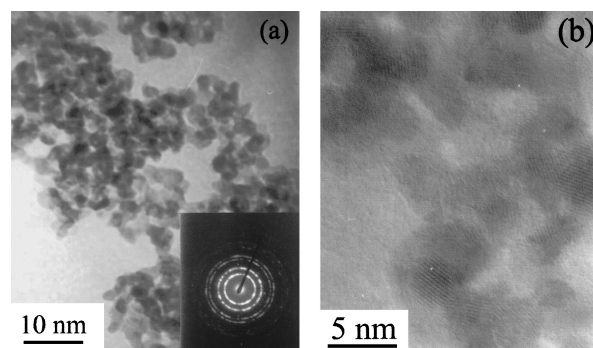


Figure 2. TEM image (a) and HREM image (b) of the powders prepared by the sol-gel method with the citric acid as complexing agent. The calcination temperature: (a) 573 K, (b) 773 K.

are in accordance with the spacings of [110], [101], and [211] of tetragonal phase SnO₂, coinciding with the XRD result. Shown in Figure 2b is the HREM image of the particles calcined at 773 K for 2 h, many crystals of about 5 nm with clear lattice strings can be seen. The connected crystals form a random network, in which are many various nanosized holes. This structure can be called a "nano-sponge structure." This microstructure leads to a very high rate of interface and surface. The particles are almost monodispersed and show low degree of agglomeration, which is also in agreement with the result previously discussed. No residual C element of the citric acid shown in the EDS indicates that the organic complexing agent had almost been combusted at this temperature.

As shown from the SnO₂ particles prepared, the sol-gel method can control the growth and agglomeration of the nanoparticles by using the citric acid as complexing agent. The particles obtained are small and monodispersed. While the particles synthesized by the direct precipitation method are relatively larger and have a high degree of agglomeration.

In summary, SnO₂ nanoparticles were prepared by a novel sol-gel method starting from granulated tin. The sizes of the particles are about 3 to 5 nm. When used as gas sensors, the sensitivity may be greatly increased.

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