Synthesis and Controlling the Morphology of SnO₂ Nanocrystals via Hydrothermal Treatment

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SnO₂ nanocrystals were synthesized via a hydrothermal method with and without a pre-addition of various surfactants. Powders were characterized by TEM for their particle size and morphology. The size and morphology of SnO₂ nanocrystals was controlled by hydrothermal synthesis. Tin oxide nanorods with a high aspect ratio were produced by hydrothermal treatment even without any surfactant addition when the hydrothermal treatment was made under a nitrogen atmosphere of about 40 atmosphere pressure. The size of these nanorods can be controlled by the temperature and time of the synthesis temperature. The addition of surfactants such as AOT and CTAB resulted in a drastic change in grain morphology from nanorods to spherical shaped particles with decreased particle size.

Introduction

Semiconductor gas sensors have been widely used as domestic and industrial gas detectors for gas-leak alarm, process control and pollution control. Among the n-type semi-conducting oxides SnO₂ is currently preferred because of its good chemical stability and its high sensitivity at low operating temperatures. The reaction between surface oxygen species and the reducing gases is of importance for gas sensitivity (1,2). The gas sensor is usually fabricated in the form of thick porous film in order to take advantage of a high surface to volume ratio that is an important factor for high performance sensor. Gas sensitivity of these materials is influenced by many factors such as the operating temperature, microstructure of the powder used for sensor fabrication and sensor geometry. The method of preparation, the deposition and the thermal treatment of the gas sensitive material determine the performance of gas sensor. Xu et al (3) studied the effect of particle size of SnO₂ sensors on the sensor’s sensitivity and found that the gas sensitivity of SnO₂ sensors to H₂, CO and I-C₄H₁₀ increases with the decrease of crystallite size in the range below 10 nm. They proposed that when particle size in the SnO₂ sensors are smaller than the Debye length, the whole of the grains themselves can be reduced, inducing the inverse change of particle size and gas sensitivity. Further the surface area of a semiconductor oxide increases as the grain size decreases. Higher surface area means that more surface active sites are available to react with the target gas molecules resulting in higher sensitivity of the sensor (4). Nanocrystalline powder provides more surface sites for more oxygen to be adsorbed and contacted with the gases, resulting in an extremely fast response. Hence most of the present research is directed towards preparation of nanocrystalline powders by various techniques, where due to the
high surface/bulk ratio, the whole volume of the material is expected to be affected by the gas atmosphere.

A variety of methods such as sol gel, chemical vapor deposition magnetron sputtering, evaporation of elemental tin in an oxygen atmosphere, decomposition of the organometallic precursor, hydrothermal synthesis and sonochemical method have been used to prepare SnO₂ particles and films. The method of synthesis influences the properties of obtained powder, particularly the shape, size, crystal morphology and the degree of crystallinity. The hydrothermal method with an aqueous solvent as a reaction medium is environmentally friendly because the reactions are carried out in a closed system. Hydrothermal synthesis involves use of water as a solvent at elevated temperatures and pressures in a closed system and certain properties of the solvents such as density, viscosity and diffusion coefficient change. The advantages of hydrothermal method over other solution routes, is that the final product readily forms at a low temperature without calcinations. Fine crystallites of the desired phase with excellent composition, morphology control, powder reactivity and purity can be obtained using hydrothermal method. It has been reported recently that hydrothermal treatment enhances the thermal stability and gas sensitivity of tin oxide (5-7). A hydrothermal treatment of tin hydroxide suspension in ammonia solution gave rise to a sol suspension dispersing nanoparticles of SnO₂ with a narrow particle size distribution. In addition the SnO₂ powder derived from the sol suspension was very resistant to grain growth at elevated temperatures. The mean crystallite size of tin oxide powder derived from 1.8 % sol suspension was about 7 and 13 nm even after calcinations at 600º and 900ºC respectively (5-7). Nanocrystalline SnO₂ (3 nm) was synthesized by a Sn/H₂O₂/H₂SO₄ hydrothermal oxidation at 50ºC (8), non agglomerated spherical particles were obtained. SnO₂ nanorods have been prepared using CTAB as template having SnCl₄ and NaOH at 160ºC for 12 hours (9).

In the present work, we have investigated the synthesis of SnO₂ powder via a hydrothermal method with and without a pre-addition of various surfactants. X-ray diffraction and transmission electron microscopy were used to get information regarding the particle size and morphology. The hydrothermal treatment made under a nitrogen atmosphere of about 40 atmosphere pressure resulted in formation of nanorods with a high aspect ratio, even without addition of any surfactant. The size of these nanorods depended on the temperature and time of the synthesis temperature. Further, the effect of AOT or CTAB surfactant addition on hydrothermally synthesized tin oxide powder was investigated.

**Experimental**

Six batches of SnO₂ powders were synthesized. Batch I SnO₂ was prepared in a conventional technique of homogeneous precipitation. 0.1 mol SnCl₄.5H₂O was dissolved in deionized water (DI), pH was maintained to ~7 using liquid ammonia diluted with water. The resulting precipitate was washed 6-8 times with ammonium nitrate solution till no chlorine is detected in silver nitrate test. The precipitate was further washed with a mixture of ethanol and water to remove NH₄⁺ and NO₃⁻ ions. This precipitate is dried in the simple oven, calcined at 600ºC for 3 hours. In preparation of batch II, the method is modified. Tin oxide hydrosol was prepared by dissolving the fully washed (Cl⁻ removed) precipitate (as batch I) in ammonia added water (pH ~10). Heating this solution at 80ºC
resulted in the formation of transparent gel, named as hydrosol in the present work. This gel was heat treated at 80-100°C to complete dryness to obtain batch II powder and this powder was than calcined at 600°C for 3 hours.

To prepare batch III and Batch IV powders, the hydrosol prepared as in batch II was treated at 180°C and 250°C for 4 hours hydrothermally. An extra pressure of about 40 atm was provided with nitrogen gas cylinder before starting the experiment. The pressure increased during hydrothermal treatment but was maintained at about 60 atm pressure. After hydrothermal treatment, the solution was heated to dryness to obtain a white powder, and similarly calcined at 600°C for 3 hours. For batch V and VI, CTAB (Cetyl trimethyl ammonium bromide) and AOT (Dioctyl sodium sulfosuccinate) surfactants were added to the hydrosol (prepared as in batch II) solution before the hydrothermal heating. 1gm surfactant was added for 50 ml water. After hydrothermal heating at 180°C for 4 hours, the liquid (gel) was dried at 80°C to obtain a powder, and subsequently calcined at 600°C for 3 hours. Calcined powders were characterized by X-ray powder diffraction (XRD) in 20 range from 20 to 70° using Bruker Analytical X-ray diffractometer equipped with graphite monochromatized CuKα radiation (λ=1.5418Å). The morphologies and dimensions of the powders were observed by transmission electron microscopy (TEM), which were taken on a JEOL model -200cx using an accelerating voltage of 200 KV.

**Results and Discussion**

SnO₂ powders prepared from conventional, hydrosol route and hydrothermal routes with and without surfactant presence (batch I to batch VI) were similarly calcined in air at 600°C for 3 hours. The XRD diffraction peaks were obtained at nearly the same positions for all the powders. All main peaks belong to cassiterite (tetragonal) phase of SnO₂ material. The width of the reflections were considerably broadened indicating small crystallite size for these powders. The average crystallite size was determined from half peak width for (110) crystalline plane and yielded 27 nm, 7 nm for batch I and batch II powders using the Sherrer equation. Crystallite sizes after hydrothermal treatment of the sol for batch III and IV were about 10 nm. Crystallite size for surfactant added sol batches V and VI were 9 nm and 7 nm respectively.

The particle size and powder morphology was determined by TEM. As shown in Fig.1 (a,b), the powder prepared by conventional route showed a wide distribution in crystallite size with crystallite size variation from 5 nm to 30 nm, with agglomerated grains. The agglomerates however consisted of primary crystallites having smaller diameter. As compared to this the powder prepared by hydrosol route, Fig. 1 (c,d), consisted of non-agglomerated particles of uniform size with average particle size of 7 nm. As observed from the micrograph, the particle size distribution for batch II powder is comparatively narrow.

Fig 2 (a,b) shows the microstructure of hydrothermally treated powder at 180°C. SnO₂ powder prepared by hydrothermal treatment showed a rod/plate like morphology. The length and aspect ratio of the SnO₂ nanorods were about 5. The diameter of the rods increased on increase in hydrothermal treatment temperature (fig.2 c-d), but the aspect ratio of the rods decreased. The nanorods prepared by hydrothermal treatment showed almost flat ends.
Fig. 1 TEM microstructure of SnO$_2$ powder (a,b) conventional route and (c,d) hydrosol route.

Fig. 2. TEM microstructure of SnO$_2$ powder by hydrothermal route (a,b) 180$^\circ$C and (c,d) 250$^\circ$C.
Fig. 3 shows the particle size and shape morphology of powders after surfactant addition. The surfactant addition plays an important role on the formation of the precursor and subsequent tin oxide grain growth as evident from the TEM micrographs for these six SnO$_2$ batches prepared under similar conditions. The grain morphology after surfactant addition changes from rod to sphere shape as observed in figure 3 (a-d). The grains (particles) were non-agglomerated or loosely agglomerated having a grain size of about 10 to 15 nm. The AOT as well as CTAB addition decreased the grain size as compared to the powder without surfactant addition. Similar results were obtained from XRD investigations. It appears that the presence of anionic surfactant like AOT as well as cationic surfactant like CTAB are affective in restricting the grain growth.

The grain growth under hydrothermal conditions is generally assumed to proceed via a dissolution-recrystallization mechanism, in which hydroxides dissolve in water and then reprecipitate as insoluble ceramic oxide particles (10). As a result smaller or less stable grains are dissolved and deposited on larger or more stable ones. With the addition of NH$_4$OH to tin chloride solution, Sn(OH)$_4$ is precipitated upto pH of about 7, this precipitate can be dissolved back on further addition of NH$_4$OH solution for pH higher than 10. Under hydrothermal treatment at high temperatures, SnO$_2$ particles are formed by the process of nucleation, precipitation, dehydration and growth between the ions and ion groups on the interfaces of the nuclei. In the present work, the nanorod like structure was observed after calcinations of the dried colloidal sol like liquid after hydrothermal treatment. The reasons for the growth of one dimensional rod like structure in the present case may be different than the formation of nanorod like structure generally observed for
materials like ZnO, and is explained by Ostwald ripening mechanism or the oriented aggregation mechanism. In an earlier report, SnO₂ nanorods were prepared by hydrothermal treatment in the presence of surfactant CTAB, which played as a template directed role (10). Tin oxide nanowires were formed, by refluxing the ethylene glycol solution of SnC₂O₄.2H₂O and PVP (11). Chen et al. (12) obtained single crystal SnO₂ nanorods through hydrothermal process using a mixture of water + ethanol, or pure ethanol as solvent in presence of CTAB. The water ethanol mixture as a reaction media was assumed to allow a slow nucleation and growth at low interfacial tension conditions which favors the generation of c-elongated anisotropic SnO₂ nanocrystals, enclosed by the stable (110) facets. SnO₂ nanowhiskers were formed using SnCl₂.2H₂O, CTAB and Na₂CO₃ on hydrothermal heating at 200°C in the autoclave charged with argon (13). In all these methods, CTAB was assumed to play an important role to direct the one-dimensional growth. In contrast, in the present work, a tin oxide hydrosol was used as precursor and a nitrogen atmosphere was maintained during the hydrothermal synthesis. The properties of hydrothermally synthesized powders, in general, depend on the synthetic conditions, such as the pH, temperature, solvent etc. In earlier work, where nanorods were obtained on addition of CTAB, instead of ammonium hydroxide, NaOH was used. In other work, an aqueous Na₂SnO₃.3H₂O and CTAB solution on addition with HCl at pH of 1.7 to 11, produced mesoporous tin oxide material having high surface area (15). Synthesis of mesoporous tin oxide was reported on addition of surfactants CTAB as well as AOT (16-18). Accordingly, the effect of surfactant will depend on the organic-inorganic interaction, mainly $S^+I^-$, and is dependent on many factors, such as the solution pH, concentration of surfactant, temperature, etc. Interaction at the interface between organic/inorganic phase, determines the structure directing effect of the organic surfactant on the inorganic component. Depending on the nature of the surfactant, size of the head group, various interactions with different strength can occur, causing a large variation in particle size of the powders made from various surfactants. As mentioned earlier, according to present investigation, the atmosphere during hydrothermal synthesis affected the powder morphology. When hydrothermal synthesis was done in air, spherical particles were obtained. Under the presence of nitrogen atmosphere, nanorods were observed in the calcined powder. According to the known theory of surfactant affect, it can be speculated that, when powders were prepared in presence of surfactants, CTAB as well as AOT, the precipitated powders were coated by a surfactant overlayer, the growth of powder is affected since the ions have to diffuse through the surfactant overlayer, which causes a reduction in grain growth. This reduction in grain growth causes the formation of spherical particles instead of nanorods, even in nitrogen atmosphere. The exact mechanism on which the nanorod shape is obtained in nitrogen atmosphere is difficult to determine at present.

As mentioned earlier, the important factor associated with the sensing properties of the prepared SnO₂ thick film is the grain size and geometry of connection. For grain sizes much less than 20 nm the sensitivity to a reducing gas is significantly increased, as the grains will be depleted of electrons and the gas response is related to intergrain conduction. Further improvement in the response may be obtained if the depletion layer thickness is close to the radius of the grains, typically measured to be about 6 nm (3). In the powder prepared by hydrothermal method the diameter of the nanorods is less than 20 nm. The affect of surfactant was found to reduce the grain size as well as the one-dimensional growth. Anionic surfactant AOT was more affective in reducing the grain growth as compared to the cationic surfactant CTAB. The use of such powders may thus
be advantageous for gas sensor applications in enhancing the gas sensitivity as well as response time.

**Conclusion**

Nanocrystalline tin oxide powders were prepared using hydrosol and hydrothermal route. Tin oxide nanorods were synthesized by hydrothermal treatment even without any surfactant addition. The hydrothermal treatment made under a nitrogen atmosphere of about 40 atmosphere pressure resulted in formation of nanorods with a high aspect ratio. The size of these nanorods can be tuned by the temperature and time of the synthesis temperature. The addition of AOT as well as CTAB surfactant resulted in a drastic change in grain morphology, the grain morphology changed from nanorods to spherical shaped particles with decreased particle size. The decrease in crystallite size was more on addition of AOT as compared to CTAB.

**References**