

Preparation of SnO₂ Powders by Modified Polyol Synthesis Using 1, 2-Propanediol and Calcination

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Abstract. SnO₂ powders were prepared using a modified polyol synthesis method and subsequent calcinations. Well-dispersed spherical 2SnO·(H₂O) particles could be synthesized at room temperature through the modified polyol method using tin (II) 2-ethylhexanoate as the precursor, 1,2-propanediol as the solvent, PVP as the capping agent, and sodium borohydride as the reducing agent. The 2SnO·(H₂O) nanoparticles agglomerated to form larger particles during the drying step, and most of these larger nanoparticles coalesced with one another. Finally, these 2SnO·(H₂O) nanoparticles were successfully transformed into the SnO₂ phase by calcination for 1 h at 500 °C.

Introduction

Tin oxide, an n-type wide bandgap semiconductor, is being explored for use as a catalyst and in various devices such as gas sensors, transparent conductive films, optoelectronics devices, and electrodes [1-11]. In most applications, tin oxide nanoparticles, which have a high surface-to-volume ratio, exhibit improved properties. For example, the use of nanocrystalline SnO₂ results in improved performance when employed in gas sensing applications and as an anodic material for batteries [1,2,4,10]. Moreover, coatings prepared using fine SnO₂ particles of well-controlled sizes may lead to the development of novel transparent conducting films in the coming years. The solution approach to fabricating transparent conductive coatings using SnO₂ nanoparticles is much more cost effective than are vacuum deposition techniques such as chemical vapor deposition (CVD) and physical vapor deposition (PVD).

A number of methods have been suggested for synthesizing SnO₂ nanoparticles, including sol-gel processes and microemulsion-, solvothermal-, hydrothermal-, sonochemical-, microwave radiation-, and spray pyrolysis-based techniques [5,12-18]. However, fabricating transparent conductive coatings via the solution approach among these synthesizing techniques can be a time-consuming process. For example, Lee et al. reported having to repetitively spin coat for up to 10 times to obtain coatings ~1 μm in thickness by a sol-gel method [19]. Hence, methods based on the spin or dip coating of solutions containing well-dispersed SnO₂ nanoparticles can be viable as low-cost alternatives for fabricating transparent conductive coatings.

In this study, SnO₂ nanoparticles were synthesized through a wet process. Because SnO₂ nanoparticles could not be synthesized directly, the initially synthesized nanoparticles were calcined in air.

Experimental

The modified polyol process entailed the decomposition of the metal precursor and reduction of the metal ions in a solvent. Tin(II) 2-ethylhexanoate ([CH₃(CH₂)₃CH(C₂H₅)CO₂]₂Sn, ~95%) and sodium borohydride (NaBH₄, 99.99%) were employed as the precursor and reducing agent, respectively. The reducing agent was dissolved in 1, 10-propanediol (99%, Aldrich Chemical Co.), unlike the liquid tin(II) 2-ethylhexanoate. In this process, polyvinyl pyrrolidone (PVP, molecular weight: 1300000, Aldrich Chemical Co.) as a capping agent was also dissolved into the 1, 10-propanediol solution to suppress agglomeration between the synthesised NPs. The PVP was initially added until the viscosity of the solution became 100 mPa·s. Other chemicals except 1,10-propanediol and PVP were supplied by Sigma-Aldrich Co. and used as-received without further processing or purification.

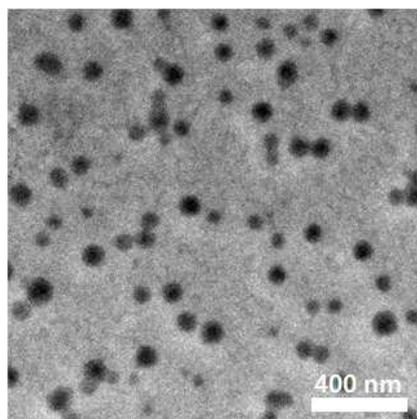


Fig.1. TEM micrograph showing the nanoparticles synthesized using tin(II) 2-ethylhexanoate as the precursor and 1, 2-propanediol as the solvent.

Nanoparticles were synthesized in air at room temperature by injecting tin(II) 2-ethylhexanoate into the solution containing sodium borohydride and PVP in 1,10-propanediol. To prepare the solution, 2 g of sodium borohydride and 1 g of PVP were dissolved completely in 100 ml of 1,10-propanediol at room temperature. Then, 2 ml of tin(II) 2-ethylhexanoate was directly injected into the 1,10-propanediol solution using a dispenser at the rate of ~ 4.5 ml/min. The 1, 10-propanediol solution was continuously stirred using a magnetic bar from the moment of injection for 120 min.

The sample for transmission electron microscopy (TEM, Tecnai G² F30ST, FEI Company) which was performed to elucidate the morphology and size distribution of the synthesized nanoparticles, was prepared by dropping a few drops of the solution of the nanoparticles in 1, 10-propanediol on to copper grids coated with carbon film. The microscopy was carried out at 300 kV.

Because drying of 1, 10-propanediol takes a long time owing to its low volatility, dried nanoparticles were prepared by carrying out a drying step using a vacuum chamber maintained at room temperature after a repetitive solvent exchanging step with methanol. The solvent exchanging step involved using a centrifuge. The centrifugation was carried out for 15 min at 4000 rpm during each solvent-exchanging step and the solution was condensed in the last cycle.

The dried NPs were used for scanning electron microscopy (SEM, Hitachi S model, Hitachi Ltd.) and X-ray diffraction (XRD, X'pert PRO-MPD, PANalytical) studies. XRD was conducted in the 2θ range $20\text{--}90^\circ$ using Cu-K α radiation. Additionally, the nanoparticles were calcined at 100°C and 500°C with a tube furnace under ambient air. Identity of the calcined nanoparticles was reconfirmed by XRD.

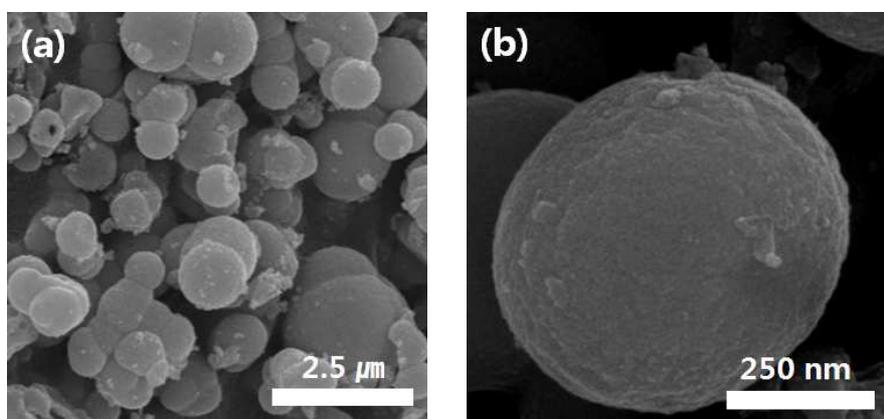


Fig.2. (a) Low- and (b) high-magnification SEM micrographs of the synthesized nanoparticles after they had been dried.

Results and Discussion

Fig.1 shows a TEM image of the nanoparticles chemically synthesized at room temperature using tin (II) 2-ethylhexanoate as the precursor and 1, 2-propanediol as the solvent. Well-dispersed spherical particles with diameters ranging from several tens of micrometers to 100 micrometers were observed.

The SEM images of these particles taken after they had been dried are shown in Fig.2. The dried nanoparticles agglomerated into larger spheres, and these spheres were between several hundreds of nanometers and a few micrometers in size. Hence, it was confirmed that the synthesized nanoparticles agglomerated during the drying process, resulting in the formation of larger particles. This agglomeration, during drying, of nanoparticles capped with polyvinylpyrrolidone (PVP) has been reported previously as well [20]. The agglomerated particles were found to be not porous, but dense, as can be seen from Fig.2(b).

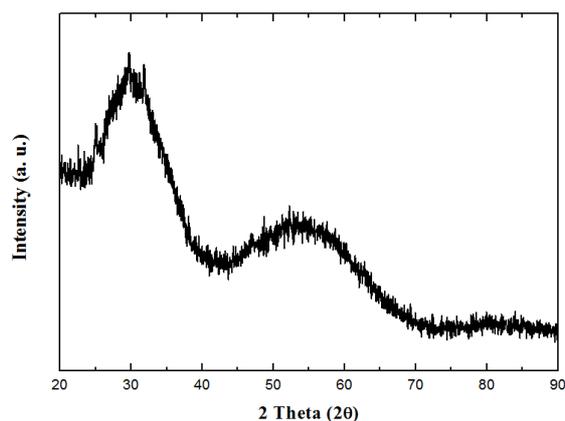


Fig.3. XRD patterns of the chemically synthesized nanoparticles after they had been dried.

Fig.3 shows the XRD patterns of the dried nanoparticles synthesized using the modified polyol synthesis method. Although the broad peaks observed at $\sim 30^\circ$ and 55° were indicative of low crystallinity and nanosized grains, the peaks could be indexed as belonging to $2\text{SnO}\cdot(\text{H}_2\text{O})$. Despite using an identical precursor, a similar synthesis method that employed a different solvent (diethylene glycol) has resulted in the formation of pure Sn nanoparticles [21]. Therefore, the type of solvent used in the modified polyol synthesis method is surmised to be the key parameter in determining whether the tin or the tin oxide phase is formed.

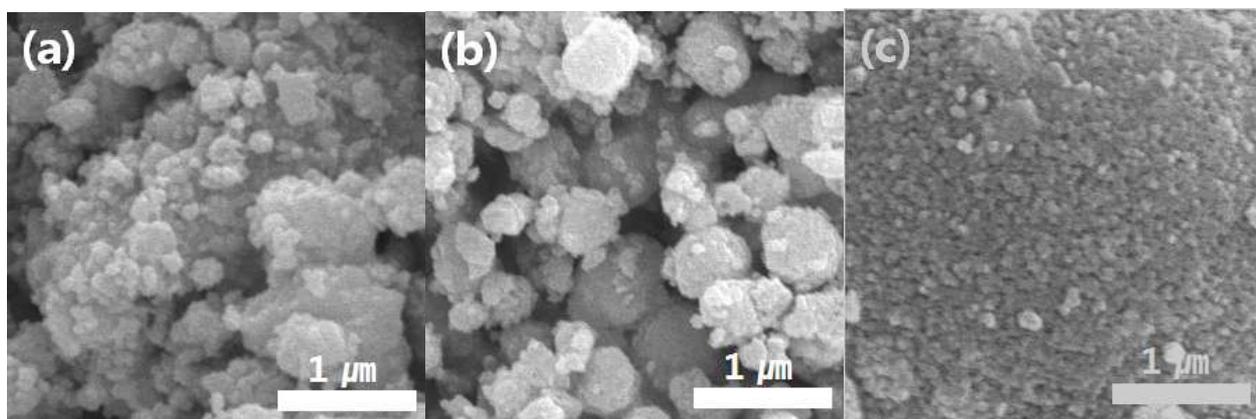


Fig.4. SEM micrographs of the various dried nanoparticles synthesized using tin(II) 2-ethylhexanoate as the precursor and high-viscosity 1,2-propanediol solutions of PVP of different molecular weights. The molecular weights of PVP were (a) 10000, (b) 55000, and (c) 1300000.

The effects of the molecular weight of PVP and the amount of PVP added on the synthesis of the nanoparticles were investigated in detail. Fig.4 shows the SEM images of the dried nanoparticles synthesized using PVP of different molecular weights with the viscosity of the 1,2-propanediol

solution containing PVP being as high as 237 mPa·s. The TEM images of these nanoparticles could not be observed owing to the presence of an excessive amount of PVP. However, it could be seen from Fig.4 that the average size of the agglomerated particles after drying increased with an increase in the molecular weight of PVP. This suggests that using PVP of a high molecular weight, which corresponds to a longer-chained structure, results in stronger interactions between the nanoparticles during the drying stage owing to Van der Waals forces. However, the cell particles, which coalesced to form the larger agglomerated particles, were observed to be just several tens of nanometers in size and smaller than those shown in Fig.1. Therefore, an increase in the amount of PVP added induced both a decrease in the size of the chemically synthesized nanoparticles and an increase in the size of the agglomerated particles after the drying step, depending on the molecular weight of the PVP added. The density of the agglomerated particles decreased with an increase in the amount of PVP added, although the density was largely dependent on the molecular weight of PVP.

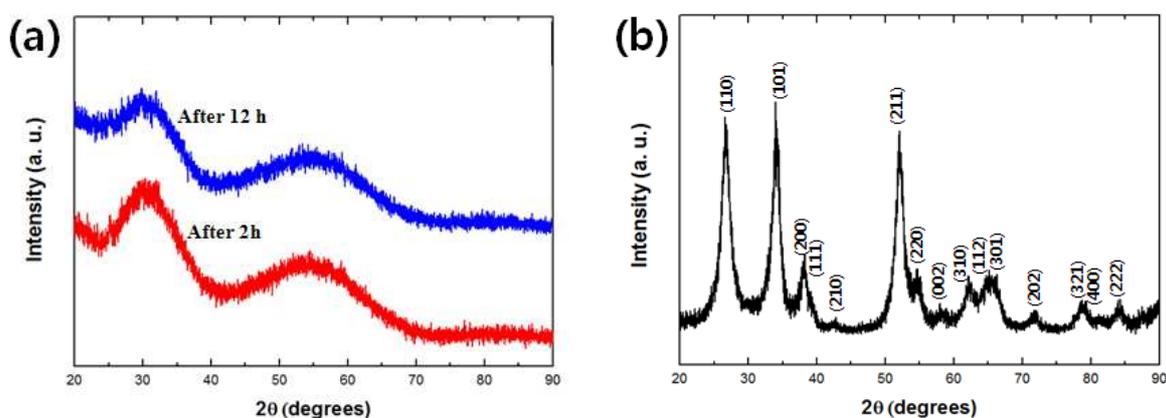


Fig.5. XRD patterns of the dried nanoparticles after they had been calcined for (a) 2–12 h at 100 °C and (b) 1 h at 500 °C.

Fig.5 shows the XRD patterns of the particles calcined under various conditions. The XRD patterns of the particles calcined at relatively low temperatures, i.e., at 100 °C, were not significantly different from those of the uncalcined ones, suggesting that the $2\text{SnO}\cdot(\text{H}_2\text{O})$ phase was still present. However, calcination at higher temperatures, i.e., at 500 °C, resulted in the XRD patterns of the calcined particles being markedly different. In addition, the patterns could be attributed to the SnO_2 phase, indicating its presence. The color of the particles exchanged from yellow-white to grey during the calcination process. Consequently, it was confirmed that the modified polyol synthesis method and the subsequent calcinations resulted in the formation of SnO_2 powders. The use of well-dispersed solutions of these synthesized nanoparticles should facilitate the fabrication of transparent conducting films via spin or dip coating methods.

Summary

Well-dispersed spherical $2\text{SnO}\cdot(\text{H}_2\text{O})$ particles with diameters ranging from several tens of micrometers to 100 micrometers were synthesized at room temperature through a modified polyol method using tin(II) 2-ethylhexanoate as the precursor, 1,2-propanediol as the solvent, PVP as the capping agent, and sodium borohydride as the reducing agent. During the drying stage, the $2\text{SnO}\cdot(\text{H}_2\text{O})$ nanoparticles agglomerated to form larger particles, and most of these bigger particles aggregated with one another. It was indirectly observed that an increase in the amount of PVP added induced a decrease in the size of the chemically synthesized nanoparticles and the density of the agglomerated particles after the drying stage. The size and density of the agglomerated particles, observed after drying, increased with an increase in the molecular weight of the PVP added. The $2\text{SnO}\cdot(\text{H}_2\text{O})$ nanoparticles were successfully transformed into the SnO_2 phase after being calcined for 1 h at 500 °C. In conclusion, we were able to fabricate SnO_2 powders successfully using the modified polyol synthesis method and subsequent calcinations.

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