Sn에 대한 In의 조성비가 초임계 SAS공정을 이용한 ITO 나노입자 제조에 미치는 영향

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Effects of a Ratio of Indium/Tin on Preparation of Indium Tin Oxide Nanoparticles by Supercritical Anti-Solvent Precipitation Process

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Introduction

Supercritical Fluid is defined as a fluid exists above critical temperature(Tc) and critical pressure(Pc). Frequently used supercritical fluids are water(Tc=374 ℃, Pc =221 bar) and carbon dioxide.(Tc=31 ℃, Pc=73.8 bar)

Techniques to manufacture nanoparticles using supercritical carbon dioxide are Rapid Expansion of Supercritical Solutions(RESS), Supercritical Anti-Solvent(SAS), and Particle from Gas Saturated Solutions(PGSS).

SAS is the technique applied to the materials which are hard to grind or recrystallize because of the properties sensitive to temperature or pressure. The principle is to extract the solute dissolved in solution by spraying the supercritical fluid used as the antisolvent with the solution[8,9].

Indium tin oxide(ITO) is a ceramic material being used to many electronic and optical applications due to its high electrical conductivity and transparency to light in the visible region[4].

In this study, the morphology of ITO particles was investigated by a SAS precipitation method to produce size-controlled nanoparticles and to enhance productivity, uniformity and various electrical and optical properties of ITO particles. The morphological behaviors in producing ITO powders were examined by modulating the process parameters such as temperature, pressure, solution concentration, and solution feed flowrates. With these parameters, especially, the effects of solute composition were studied.

Experiments

A typical SAS experiment was started by delivering supercritical CO_2 to the precipitation chamber up to 150 bar at 50 ℃ with 20 % concentration of solution determined by the preliminary experiments as the optimum operating conditions. Then, the flowrates of ethanol used the solvent in this study and the supercritical CO_2 was regulated at 1 ml/min and 10 ml/min respectively to obtain the steady-state operating condition and to avoid the clog of the nozzle[6]. As soon as the injection of the pure liquid solvent was stopped, the solution was delivered through the nozzle at the flowrate of 1.0 ml/min with 9:1 as the solute ratio of indium to tin(In/Sn).

This stage was proceeded for 10 min or more to collect the solid particles sufficient to perform the analysis of the precipitate. This experiment finished when the solution delivery was ended. However, supercritical CO_2 was continuously delivered for 120 min to wash the residual contents of liquid solvent in the precipitation chamber and particles dissolved into the supercritical antisolvent. If this washing process is not done, particles are not formed and residual solvents are still remained in the precipitation chamber even after washing. When the washing process was completed, the CO_2 flow was stopped and the chamber was depressurized down to atmospheric pressure.

To investigate the influence of the solute ratio of In/Sn on the morphology of ITO particles, the experiments were repeated from 8:2 to 6:4[7].
A schematic representation of the SAS apparatus in this study is shown in Fig. 1.

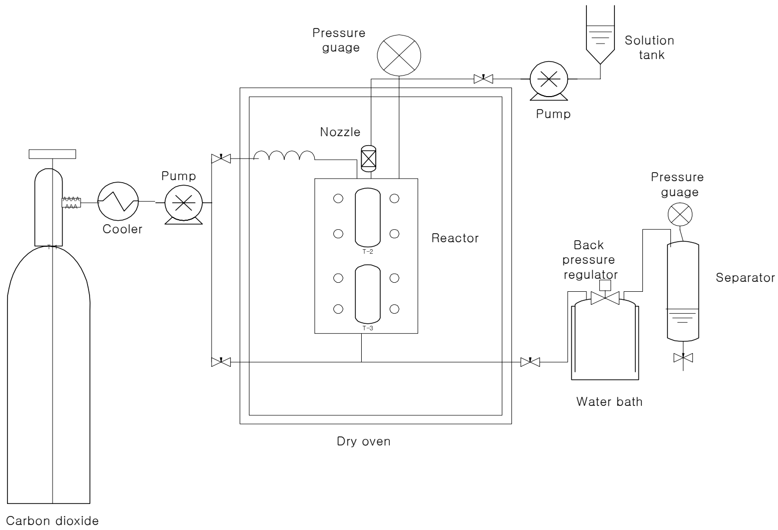


Fig. 1. Schematic diagram of SAS system.

Results and Discussion

The process of SAS micronization process depends, as in liquid antisolvent precipitation, on the solubility of the liquid solvent in the supercritical antisolvent and the fact that the solute is not soluble in the antisolvent. However, it also depends on the fast solubilization of the liquid due to the gas-like diffusion characteristic of supercritical fluids. This last characteristic is fundamental in assuring that very small particles are obtained.

According to prior authors[1-5], it is known that particle types and sizes depend on the experimental variables such as concentration of solution, temperature, pressure, feed flowrate of solution, and types of solvent etc.. The experimental conditions were also applied to this work.

From the rigorous performances of SAS processes, the pressure of 150 bar, the temperature of 50 ℃, the solution concentration of 20 %, and the solution feed flowrate of 1.0 ml/min were determined as the best conditions of the process parameters used ethanol as a solvent and 9:1 as the solute ratio of In/Sn. Under the conditions, it is confirmed that the particles were obtained about 30nm with relatively excellent uniformity.

The effects of the solute ratio of In/Sn on the morphological behaviors in producing ITO powders were also investigated. With the exception of the solute ratio of In/Sn, the process parameters optimized were fixed and the range of the solute ratio of In/Sn was applied to 9:1, 8:2, 7:3, and 6:4, respectively.

From the analyses of SEM image, the particles having the diameter about 30nm with relatively good uniformity were produced, respectively. SEM image for the ratio of 7:3 was illustrated in Fig. 2. But, from XRD analyses, ITO powders were hardly crystallized except for the ratio of 9:1. XRD traces of commercial ITO particles and prepared particles for the ratio of 9:1 and 6:4 were shown in Fig. 3.

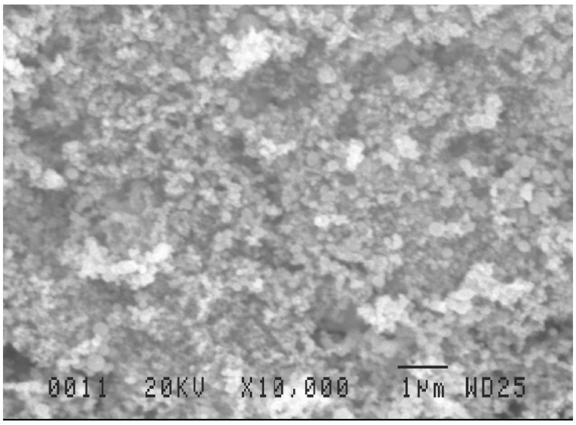
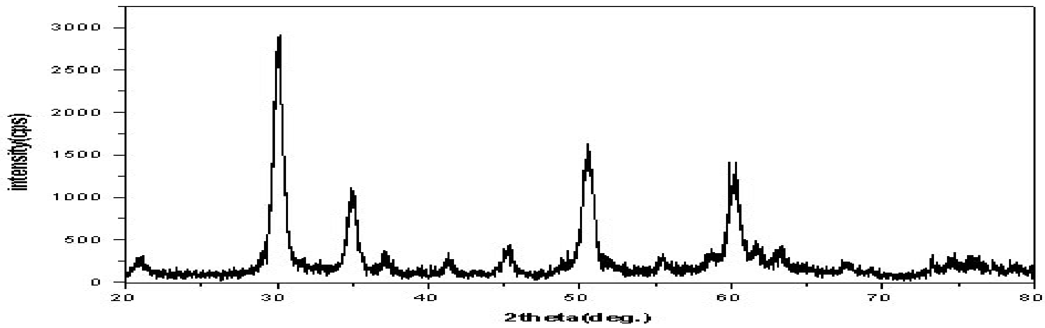
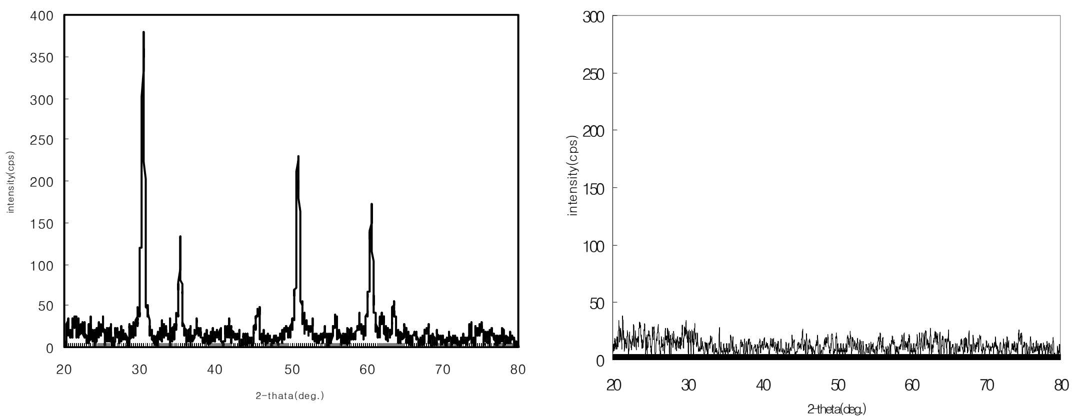


Fig. 2. SEM image of prepared particles for the solute ratio of 7:3



(a) commercial



(a) 9:1 (b) 6:4

Fig. 3. XRD trace of commercial ITO particles and prepared particles for the ratio of 9:1 and 6:4 :(a) commercial, (b) 9:1 (c) 6:4.

Conclusion

The morphology of ITO particles was studied by SAS precipitation technique recently proposed to produce size-controlled nanoparticles of various material in order to enhance productivity and uniformity.

The morphological behaviors in preparing ITO powders were examined by modulating the process parameters such as temperature, pressure, and solution concentration etc.. With these process parameters, especially, the effects of the solute ratio taken as 9:1, 8:2, 7:3, and 6:4, respectively, were also investigated.

From the detailed performances of the processes, the pressure of 150 bar, the temperature of 50 ℃, the solution concentration of 20 %, and the solution feed flowrate of 1.0 ml/min were determined as the best conditions of SAS processes used ethanol as a solvent and 9:1 as the solute ratio of In/Sn. Under the conditions, it is confirmed that the particles were obtained about 30nm with relatively excellent uniformity.

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