

Electrochemical Characteristics of Indium Tin Oxide Nanoparticles prepared by Sol-gel Combustion Hybrid Method

Accarat Chaoumead*, Woo-Jin Choi*, Dong-Hoon Lee** and Youl-Moon Sung[†]

Abstract – Indium tin oxide (In:SnO₂) nanoparticles were synthesized employing a sol-gel combustion method followed by annealing. The TG, XRD, XPS and SEM results of the precursor powders and calcinated In:SnO₂ nanoparticles were investigated. Crystal structures were examined by powder XRD, and those results show sharper intensity peak at 25.6° (2θ) of SnO₂ by increased annealing temperature. A particle morphology and size was examined by SEM, and the size of the nanoparticles was found to be in the range of 20~30nm. In:SnO₂ films could be controlled by nanoparticle material at various annealing temperature. The sol-gel combustion method was offered simple and effective route for the synthesis of In:SnO₂ nanoparticles.

Keywords: Nanoparticle film, Indium tin oxide, Sol-gel combustion method, Transparent conductive oxide

1. Introduction

Transparent conductive oxide (TCO) films are of importance for various device applications, such as solar cells, photo sensors, displays and electroluminescent devices [1-3]. The efficiency of such photo-electronic devices could be highly enhanced if porous properties are endowed to TCO electrodes due to their high surface area. The nano-structurization of TCO electrodes have attracted attention by using various fabrication process methods [4, 5]. Indium tin oxide (In:SnO₂) is one of the representative TCO materials capable of showing high optical transmittance (~ 90%) in the visible light range as well as good electrical conductivity (~2×10⁻⁴ Ωcm). The sputter deposition method has been usually utilized to fabricate the In:SnO₂ film with well-ordered dense structure, however the pore structure has not been formed during the deposition. On the other hand, sol-gel combustion method can be considered as a useful method for nanoporous structure fabrication process [6, 7], and has advantages in efficient and large-scale fabrication of a nanoparticle electrode with large internal surface area. Until now, the sol-gel combustion hybrid method has been widely adapted to synthesize various nanoparticle materials, such as TiO₂, F:SnO₂ and SnO₂ [6-8]. However, availability of In:SnO₂ nanoparticle material synthesized by sol-gel combustion hybrid method has not been fully clarified.

In this work, our aim is to develop new structural elec-

trode materials used for electrochemical cell application that have the potential to yield nanoporous In:SnO₂ materials with the uniform particle size by the sol-gel combustion hybrid method. The experimental investigation of the effects of annealing on thin porous films consisting of ITO nanoparticles has been performed. The discussion was focused on both morphology and electrochemical properties of the nanoporous In:SnO₂ materials obtained by tuning the temperature of the thermal treatment used to crystallize the materials.

2. Experimental

The In:SnO₂ nanoparticles material was prepared by a sol-gel combustion hybrid method using starting materials of high purity SnCl₄(99.99%), In(NO₃)₃·xH₂O (99.99%) and NH₄OH(50%). SnCl₄(99.99%), In(NO₃)₃·xH₂O (99.99%), and NH₄OH (50%) in water (semiconductor grade) [8]. Fig. 1 shows the flow scheme for the sol-gel combustion process employed for the synthesis of In:SnO₂ nanoparticle material. For the synthesis of In:SnO₂ nanoparticle, indium tin solution was prepared by dissolving 4.752 g of In(NO₃)₃·5H₂O and 0.648 g of SnCl₄ in 20 ml of deionized water. The quantity of metal ion in the solution was adjusted as the final oxide composition of 90:10 weight ratio of In₂O₃/SnO₂. 0.4 g of Ketjen black was added to this indium tin solution and then NH₄OH aqueous solution was added drop by drop under constant stirring until it turned to a sol at ambient condition. The bath temperature was maintained at 30°C. This sol was heated at 120 °C for 120 min to get the sol transferred into dried gel. The dried gel was calcined at various temperatures viz. 450, 500, 550, 600, 650, and 700°C. Being ignited in air at

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450°C, an auto-combustion process took place and as-burnt powder was obtained. The powder was further calcined at 700°C for 120 min in air to get the In:SnO₂ nanoparticles. In:SnO₂ nanoparticles material was examined by powder X-ray diffraction (XRD; Rigaku, Ultimaplus diffractometer D/-Max 2000). Particle morphology and size were investigated by field emission scanning electron microscope (FE-SEM; Hitachi, S-4300).

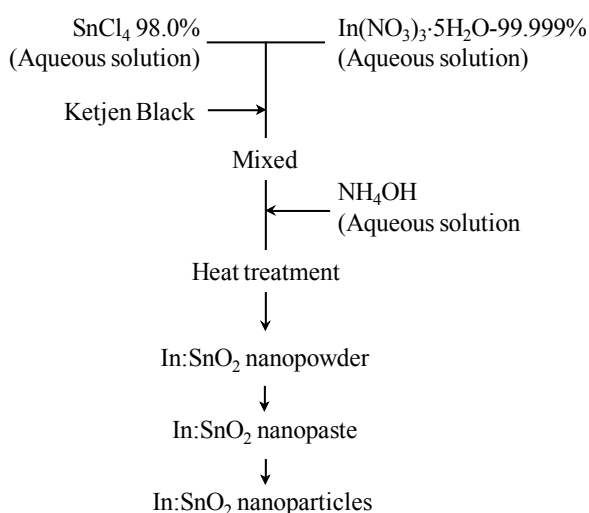


Fig. 1. Synthesis process of In:SnO₂ nanoparticles using sol-gel combustion hybrid method.

3. Results and discussion

In order to investigate the conversion of the gel into densified powder by sol-gel combustion hybrid method using Ketjen black, simultaneous thermal analysis has been done on the dried gel precursor of In:SnO₂. Fig. 2 shows the thermo gravimetric analysis (TGA) plot of the In:SnO₂ nanoparticles material. There was only one large exothermic peak at 300°C, which belongs to the formation of the In:SnO₂ nanoparticles. The TGA profile shows that the precursor is subjected to continuous mass loss in the temperature range of 300~500°C, and showing a marked slow weight loss beyond 600°C. This means that the precursor is transformed into oxide nanoparticles around 500~600°C as shown in TGA curve. In general, combustion reaction continues only a few seconds and its reaction is too violent to control in conventional combustion method [8]. The reaction, however, was not so violent in this sol-gel combustion hybrid method using Ketjen black.

Nanoparticles structure of the In:SnO₂ materials synthesized by sol-gel combustion hybrid method was examined by XRD and the result for the sample calcined at 550 °C is shown in Fig. 3. The peaks observed in the XRD pattern of 550 °C calcined sample match well with the cubic In:SnO₂ peaks [9]. The sharp diffraction peaks for the sample calcined at 550 °C indicates a high degree of crystallization in

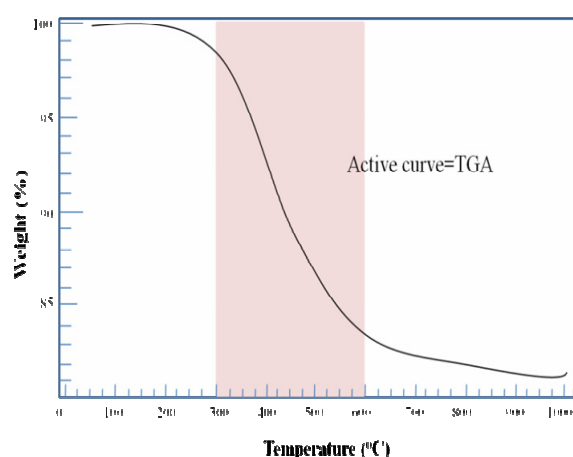


Fig. 2. TGA curve of prepared In:SnO₂ nanoparticles material between 30 and 1000 °C recorded for a heating rate of 5 °C/min.

the In:SnO₂ nanoparticles. It can be seen, from the XRD result, that for case the peak at 30.2° (2θ), the intensity of the peak increases with increasing calcination temperature and the full-width half-maximum (FWHM) widths of the peaks decreases with increasing temperature. This indicates that crystallization of the In:SnO₂ nanoparticles progresses gradually with as the treating temperature increases, and the perfect crystallization can be obtained at higher temperatures at 550°C. The calculated lattice parameter for cubic In:SnO₂ phase was 10.13F002 Å, whereas the reported lattice parameter of undoped In₂O₃ which is 10.118 Å. The particle size of the In:SnO₂ material was roughly calculated from X-ray data using Scherer's equation [10]

$$d = 0.9 \lambda / (\beta \cos\theta) \quad (1)$$

where d is average grain size, β the full-width half-maximum, λ the X-ray wave-length of Cu-K α radiation and θ the Bragg angle. Using this formula, the calculated the particle size of In:SnO₂ was in the range of 30 nm.

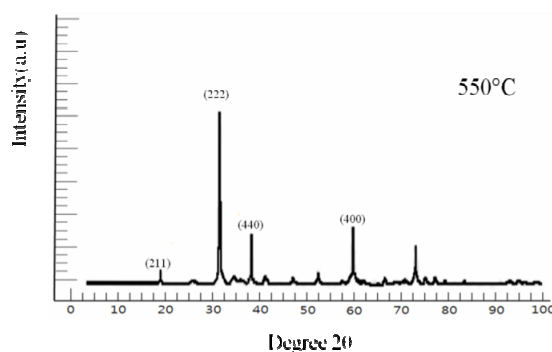


Fig. 3. X-ray diffraction pattern of In:SnO₂ nanoparticles calcined at 550 °C.

Fig. 4 and Table 1 show the Zeta-potential analysis result of prepared In:SnO₂ nanoparticle materials. Mean parti-

cle's sizes are summarized in Table 1. Mean particle's size is found to be 35 nm for S_{550} . After thermal treatment, the mean particle's size increases from 35nm for S_{550} to 150nm for S_{700} . It is clear that the particle size increases as the treatment temperature increases.

Table 1. Particle size of the In:SnO₂ nanoparticles samples.

Sample	Polydispersity	Diffusion Const (cm ² /sec)	Mean particle diameter (nm)
S_{450}	2.697e-001	1.5545e-008	25.2
S_{500}	2.394e-001	1.7583e-008	35.6
S_{550}	2.588e-001	1.4547e-008	35.7
S_{600}	2.511e-001	1.5342e-008	83
S_{650}	2.620e-001	1.5431e-008	100
S_{700}	2.738e-001	1.3663e-008	150.2

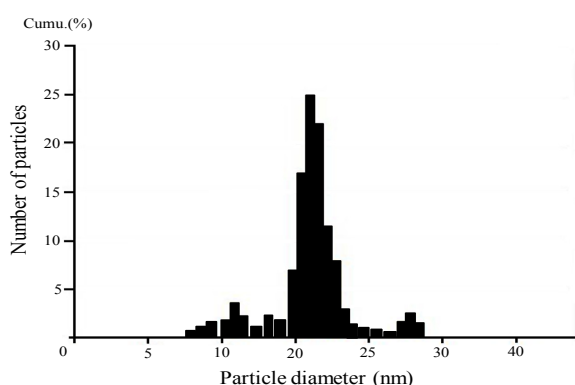


Fig. 4. Xeta-potential of In:SnO₂ nanoparticles material.

XPS measurements were carried out to confirm the In concentration in the In:SnO₂ nanoparticles sample at 550°C as shown in Fig. 5. The binding energies of the O1s, Sn_{3d₅} and In_{3d₅} photoelectron peak are at 530, 486 and 444 eV, respectively. A C1s peak at a binding energy of 285 eV is also observed on the sample. The presence of this peak is related to the fact that the samples contained Ketzen black in the sol-gel process before the XPS measurements. The binding energy of Sn_{3d₅} at 486 eV can be attributed to the Sn₂₊ bonding state from SnO₂. The Ins concentration in the In:SnO₂ sample calcined at 550 °C was below 1%.

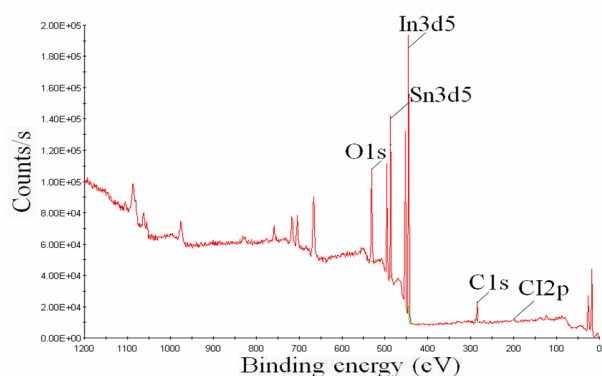


Fig. 5. XPS wide spectra of the In:SnO₂ nanoparticles prepared by sol-gel combustion method at 550°C calcinating temperature.

Fig. 6 shows an example of FE-SEM image for In:SnO₂ nanoparticles material at 550°C calcinating temperature. The In:SnO₂ nanoparticles material consists of very uniform size cuboid particles of 20~30 nm size. This is in agreement with the results obtained from the XRD analysis. Thus, the sol-gel combustion method could be employed to synthesize the In:SnO₂ nanoparticles with narrow size distribution. Table 2 shows the BET analysis result of In:SnO₂ nanoparticles. The mean pore size is found to be 20~25 nm for S_{550} .

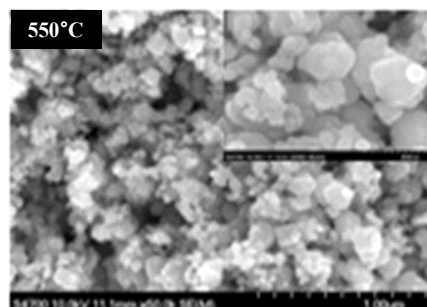


Fig. 6. FE-SEM image of In:SnO₂ nanoparticles material calcined at 550 °C.

Table 2. BET surface area, pore volume and pore size of the In:SnO₂ nanoparticles samples.

Sample	S_{BET} (m ² /g)	Total pore volume (cm ³ /g)	Mean pore diameter (nm)
S_{450}	320	0.25	9
S_{500}	292	0.24	15
S_{550}	250	0.24	22
S_{600}	220	0.23	30
S_{650}	150	0.22	45
S_{700}	90	0.22	78

4. Summary and Conclusion

In:SnO₂ nanoparticles material can be synthesized employing a new route sol-gel combustion hybrid method using Ketjen Black. The In:SnO₂ nanoparticles materials can controlled by the calcination temperature, and are optimized at 550°C calcinating temperatures. The change in particle's size with the calcinations shows that the mean size increases with increasing calcinations temperature. The In:SnO₂ nanoparticles materials have crystallite size ranging from 20nm to 30nm. The mean pore size of the sample is range of 30~35 nm. The surface area In:SnO₂ materials is reduced upon thermal treatment. The sol-gel combustion hybrid method offers a simple and effective route for the synthesis of uniform crystallite size.

Acknowledgments

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