# Effects of Doping Concentration and Annealing Temperature on Indium Doped Zinc Oxide Particles Prepared via Sol-Gel Method

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## Abstract

Doping of indium in zinc oxide (ZnO) is one of the means to increase its electrical conductivity. This study focuses on investigating the effects of indium doping concentration (In/Zn = 3%, 5% and 7%) and annealing temperature (200°C, 300°C and 450°C) on the electrical conductivity, structural, morphological and elemental properties of the indium doped zinc oxide (IZO) particles. The synthesis of IZO particles was carried out by a simple sol-gel method where sol-gel was evaporated to xerogel, heat treated and milled to form solid particles. The particles were characterized by four-point probe, X-ray diffraction (XRD), Fourier transform infrared (FTIR) and scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDX). The results obtained demonstrate an impressive increase of electrical conductivity by one order of magnitude at 5% of indium doping compared to the pristine zinc oxide (ZnO) as a result of cumulative charge carriers. Besides, an increase of annealing temperature also shows a positive effect on the electrical conductivity. XRD results show distinctive changes on crystal structure of polycrystalline wurtzite structure and its crystallite size with the change in parameters. FTIR results indicate the effects of both parameters by the presence and elimination of peaks designated for IZO functional group. The SEM-EDX analysis reveals the microstructure morphology at different parameters and validates the existence of each element according to doping concentration.

**Keywords:** indium doped zinc oxide, zinc oxide, sol-gel method, annealing temperature, indium doping concentration

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## Introduction

Zinc oxide (ZnO) is commonly used as an effective transparent conductive oxide (TCO) in solar cell, surface acoustic wave devices, spintronic devices, and blue/UV optoelectronics applications due to its well-known great optical properties and also a promising electrical properties. Besides, ZnO offers a creditable abundant material resources and non-toxicity, hence being a potential substitute of traditionally used tin oxide ($SnO_2$). There are various synthesis methods applied in production of nanocrystalline zinc oxide such as precipitation, solvothermal hydrothermal, emulsion, microemulsion, mechanochemical and etc. Amongst them, sol gel method is commonly used due to its low cost, repeatability, reliability and relatively mild conditions of synthesis method [1]. These advantages have brought some researches to practice sol gel method in synthesising ZnO particles for characterization studies and applications [2,3].

The electrical conductivity of pristine zinc oxide is basically attributed from the intrinsic defects of oxygen vacancy and zinc interstitial. However, these intrinsic defects claimed to be unstable with high resistivity, hence restricts the ZnO from being applied as electrically conductive filler. Thus in this case, extrinsic dopant of metal element Group III such as gallium, aluminium and indium may increase the particle conductivity and its functionality [4]. For that reason, ZnO has attracted many researchers to broadly study its impurity doped properties in various applications. Amongst these metal element Group III, the most studied doping elements are Ga-ZnO and Al-ZnO [5]. There are still limited studies done on the indium doping of ZnO particles due to its higher cost than aluminium. Nevertheless, indium has been a better potential for its great resistance to oxidation compared to aluminium. It is also compatible to natural fiber as it has low processing temperature that makes it suitable for low degradation temperature of kenaf [6]. Besides, study on the effects of indium doping and annealing temperature on the electrical conductivity is vital in improving the electrical properties of zinc oxide, as it correlates with the particle characteristics. Thus, this study aims to investigate the effects of indium doping concentration and annealing temperature on the electrical conductivity and the characteristics of IZO particles synthesized via sol gel method.

## Materials and Methods

### *Materials*

The chemicals used to synthesize IZO particles were analytic grades of zinc acetate dihydrate ($Zn(CH_3COO)_2 \cdot 2H_2O$), indium chloride ($InCl_3$), deionized water and absolute ethanol. All the chemicals were purchased from Polyscientific Sdn. Bhd.

### *Synthesis of IZO Particle*

The solution preparation was started by dissolving 0.1 M of zinc acetate dihydrate in 100 ml absolute ethanol. It was vigorously stirred using magnetic stirrer for 2 hours at room temperature. Then, indium chloride was added into the solution according to the concentration of 3%, 5% and 7% molar percentage (mol%) and vigorously stirred for another 2 hours at 75°C. While stirring, deionized water was added into the solution until clear solution was obtained. Then, the resulted colloidal solution was stored for 24 hours at room temperature for gelation process. Next, to form the nanocrystalline IZO, the sol-gel was dried at 80°C for 20 hours into dried solid (xerogel) before annealed at different temperatures for 4 hours in furnace. The first experiment is to study the effects of annealing temperature, where the indium concentration

was kept constant at 5% indium at the temperatures of 200, 300 and 450°C. Meanwhile, in another set of experiment, i.e., study the effects of indium concentration of 3%, 5% and 7% In/Zn, annealing temperature was kept constant at 200°C. The final solid product was ground by ball milling and sieved by 75 µm sieve to obtain fine particles and ready to be analysed.

### *Testing and Analysis*

The analyses involved in this study were electrical conductivity and IZO particles characterization. The conductivity test was carried out on IZO pallets by using 4-point probe. These pallets were formed by compressing the particles at 10 MPa by using hydraulic press. Meanwhile, characteristics of crystal structure and functional group bond of IZO particles were analyzed by X-ray diffraction (XRD) and Fourier transform infrared (FTIR), respectively. From the XRD data, crystallite size was calculated by using Scherrer's formula (1).

$$D = \frac{0.9\lambda}{\beta \cos\theta} \tag{1}$$

where $\lambda$, $\theta$, $\beta$ and D are X-ray wavelength, Bragg's diffraction angle, full width at half maximum of the peak and average crystallite size of the particles, respectively. In addition, scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX) were used to investigate the microstructure morphology and to validate the presence of related elements of indium doped zinc oxide.

## Results and Discussion

### *Structural Analysis by X-Ray Diffraction (XRD)*

The structural properties of IZO and ZnO particles were analyzed through the XRD plot shown in Figure 1. The similar XRD pattern from both IZO and ZnO as shown in Figure 1(a) are attributed to planes of hexagonal wurtzite zincite nanocrystal with preferred orientation along (101) plane at 2θ: 36.3° (JCPDS File No: 036-1451). This identical characteristic clarifies that indium doping does not alter the crystal structure of ZnO, which proves that only interstitial incorporation of $In^{3+}$ ions occur in the ZnO crystal lattice [7]. Besides, detection of peaks qualifying as tetragonal indium at the planes of (101), (202), (103), (211) and (201) (JCPDS No. 005-0642) is reported. Though, the results show a definite decrease in peak intensity of ZnO associated with the addition of indium doping. This finding indicates that crystal structure of ZnO is deformed by either the substitution or interstitial of $In^{3+}$ ions in the ZnO host lattice, which causes lattice expansion due to larger ionic radii of $In^{3+}$ ions (80 picometer) as compared to $Zn^{2+}$ (74 picometer) [8]. The same phenomenon was observed regardless of the indium doping concentration.

Meanwhile, Figure 1(b) shows the XRD pattern of IZO particles formed at different annealing temperatures. The results suggest that the increase of annealing temperature results in distinct formation of crystal structure of hexagonal zincite at planes (101), (002), (101), (102), (110), (103), (200), (112) and (201) which also with the preferred orientation along (101) plane at 2θ: 36.3° (JCPDS File No: 036-1451). These planes start to grow at annealing temperature of 300°C which indicates an increase of crystallinity and diminishing of amorphous structure in the particles.

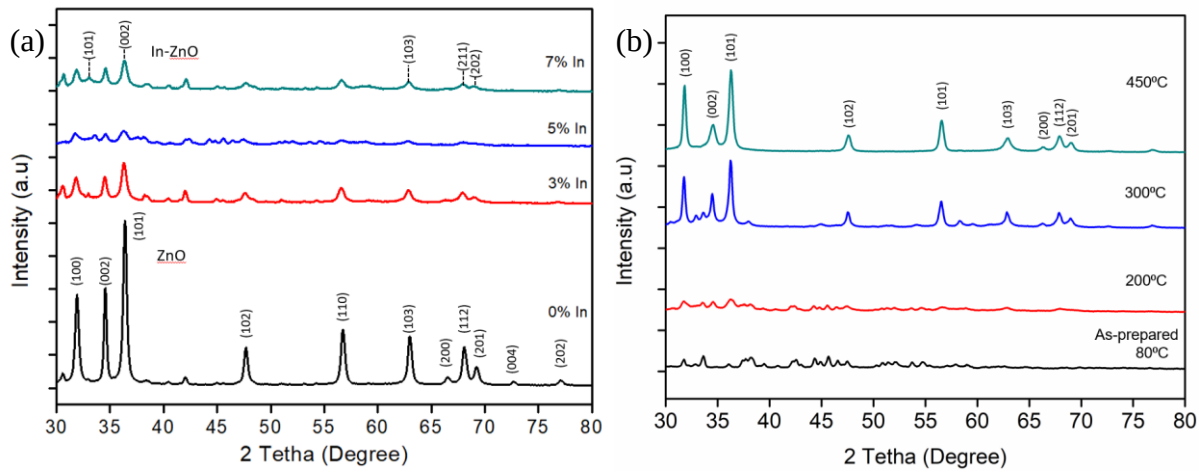


**Figure 1: XRD patterns for IZO with different (a) effect of indium doping concentration at constant 200°C and (b) effect of annealing temperature at constant 5% indium doping.**

Further analysis on XRD data is plotted in Figure 2 which illustrates the effect of (a) indium doping concentration and (b) annealing temperature on the crystallite size and full-width at half-maximum (FWHM) at which the crystallite size is inversely proportional to the FWHM value. Based on the result obtained, crystallite size increases from 22.23 nm to 29.61 nm with the increasing concentration of indium doping from 3% to 5% but decreases to 25.54 nm after further increase in doping concentration to 7% (Figure 2(a)). Meanwhile, un-doped ZnO gives value of 25.41 nm crystallite size, which is smaller than indium-doped ZnO and verifies the increase of crystallite size by addition of indium doping. However, the decrease of crystallite size on further doping of 7% indium is probably due to the deterioration of particles crystallinity associated to compression stress resulting from the further occupation of indium ion in zinc oxide interstitial sites [9].

Figure 2(b) demonstrates the increase of crystallite size from 25.38 nm (80°C) to 29.61 nm (200°C) and 29.63 nm (300°C). This behavior implies that as the annealing temperature rises, more kinetic energy is gained by the atoms hence contributes to thermal expansion. Due to this thermal expansion, the particles merge to form larger crystallite [10]. However, as the temperature rises to 450°C, the crystallite size decreases to 22.23 nm. It is believed that as more sufficient thermal energy obtained by the atoms at annealing temperature of 450°C, atomic rearrangement within the IZO particles occurs. At this point, the atoms may move to any favorable space within the crystalline, hence results in a decrease of its crystallite size [11,12].

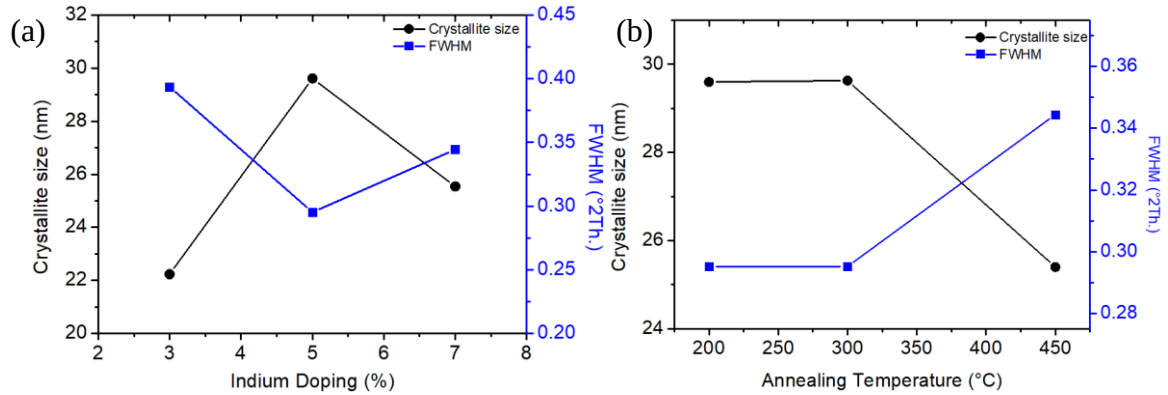


**Figure 2: The crystallite sizes and FWHM of preferred peak (101) as the (a) indium doping concentration and (b) annealing temperature, are varied.**

### *Fourier Transform Infrared (FTIR) Analysis*

Figure 3 illustrates the FTIR results for IZO with (a) different indium doping concentration and (b) different annealing temperature. The peak of 400-700 $cm^{-1}$ in Figure 3(a) and (b) corresponds to Zn-O wurtzite structure, which verifies the presence of zinc oxide bond on the particles. At the same time, there is a strong peak at 650-700 $cm^{-1}$ which possibly indicates hydroxyl bond with zinc (Zn-OH). Besides, the hydroxide bond associated peaks also appear at 1330-1420 $cm^{-1}$ and 3000-3100 $cm^{-1}$ which match with hydroxide O-H bending and O-H stretching, respectively and is believed from the residual of used raw material or adsorption of moisture on the particles. Meanwhile, weak peak at 1050-1085 $cm^{-1}$ signifies the C-O stretching of primary alcohol from the sol-gel solvent. The peak at 1550-1600 $cm^{-1}$ represents stretching and bending vibration of symmetric C=O modes originated from the residual of used chemicals.

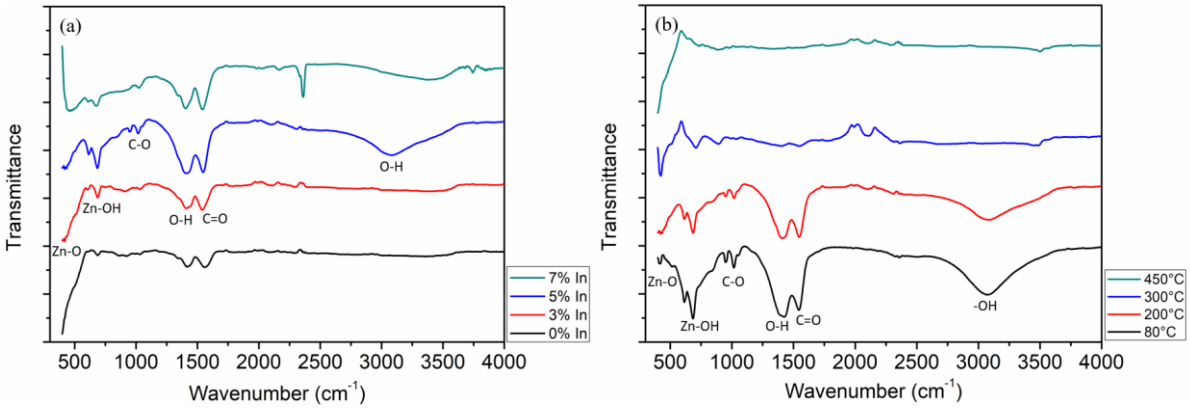


**Figure 3: FTIR spectra for IZO with (a) different indium doping concentration and (b) different annealing temperature.**

FTIR pattern from the Figure 3(a) shows a distinct appearance and broad peak of hydroxide O-H bond which indicates the formation of zinc hydroxide ($Zn(OH)_2$) and indium hydroxide ($In(OH)_3$) in the particle resulting from indium doping at which hydroxyl $OH^-$ resulted from moisture or raw material were attached to $Zn^{2+}$ and $In^{3+}$ generating hydroxide O-H bond [13] in agreement of Zn-OH bond formation on the FTIR result. As the doping increases, there are more $H^+$ from the environment strongly attracted to the $O^{2-}$ anions from the resulted zinc oxide (ZnO) and creating more O-H bond which also correspond the intense peak

of O-H bond. However, as the annealing temperature increases (Figure 3(b)), the O-H bond reduces significantly due to elimination or evaporation of solvent after the heat treatment. Besides, the disappearances C-O and C=O bond are caused by elimination of raw chemicals or solvent which is mostly due to the increase of annealing temperature [14].

### *Morphological and Elemental Analysis by SEM and EDX*

### *Effect of indium doping concentration*

Figure 4 illustrates the morphological structure of IZO particles on the effect of indium doping concentration and its elemental characteristics. The SEM images show the structure of 2D nanosheet which demonstrates the existence of ZnO in all samples [15]. However, the nanosheets structure of ZnO seems to decrease as the doping concentration increases, which strongly correlates with the reduction of crystallinity of ZnO due to substitution of $Zn^{2+}$ ions with $In^{3+}$ ions. Based on grain size data from XRD, it confirms an increment of particle size as the doping concentration increases. Though, the real illustration from SEM microstructure demonstrates resulted heterogenous particle size of ZnO and IZO. Meanwhile, EDX data shows the atomic and weight percentage of each element of carbon (C), oxygen (O), zinc (Zn) and indium (In). Based on the EDX data, atomic percentage of indium doping shows approximately 3.25, 5.52 and 3.49 atomic percentage of In doping for the 3%, 5% and 7% (mol%), respectively. The result verifies the existence of indium atom in the zinc oxide particles is almost according to the doping concentration, except for 7% of indium doping, which is believed due to the non-uniform dispersion of atom and agglomeration of doping on the particles that leads to inconsistency of EDX reading.

### *Effect of annealing temperature*

On the other hand, the effects of annealing temperature on the microstructure of IZO are analyzed based on SEM micrographs in Figure 5. The microscopic images of the particles correspond to the XRD results shown in Figure 1(b). As the annealing temperature increases from 200°C to 450°C, the grain microstructure changes to a different shape; from amorphous (Figure 5(a)-(b)) to crystalline 2D nanosheet (Figure 5(c)-(d)) and then transforms to fine nanosphere particles (Figure 5(d)-(h)). This observation is in agreement to the study by Kołodziejczak-Radzimska [1]. The elimination of residual chemical and moisture by the annealing process improves the particles crystallinity and changes the microstructure.

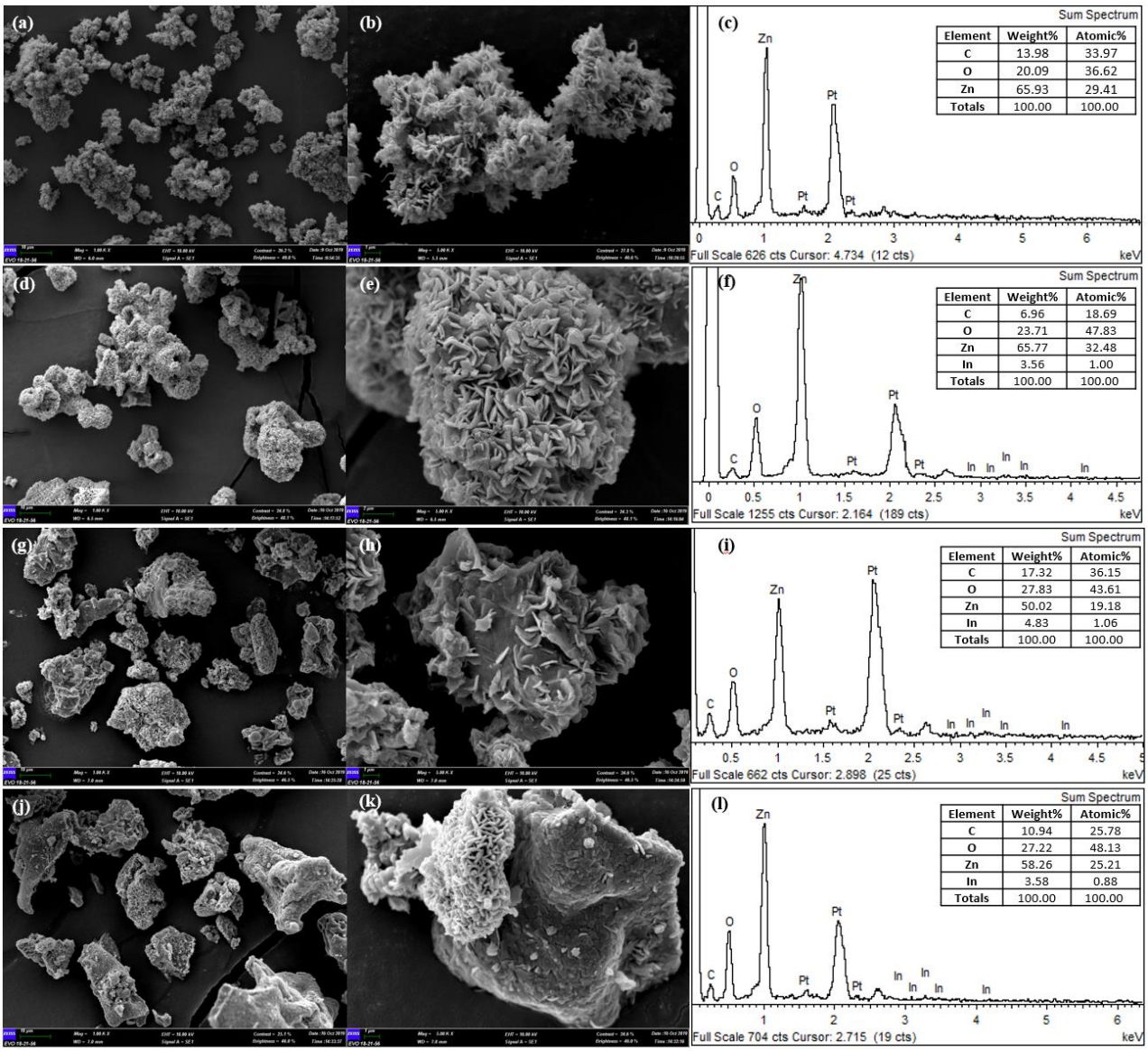


**Figure 4: SEM images (1000x and 10000x magnification) and EDX result for IZO with (a)-(c) 0% indium doping, (d)-(f) 3% indium doping, (g)-(i) 5% indium doping and (j)-(l) 7% indium doping.**

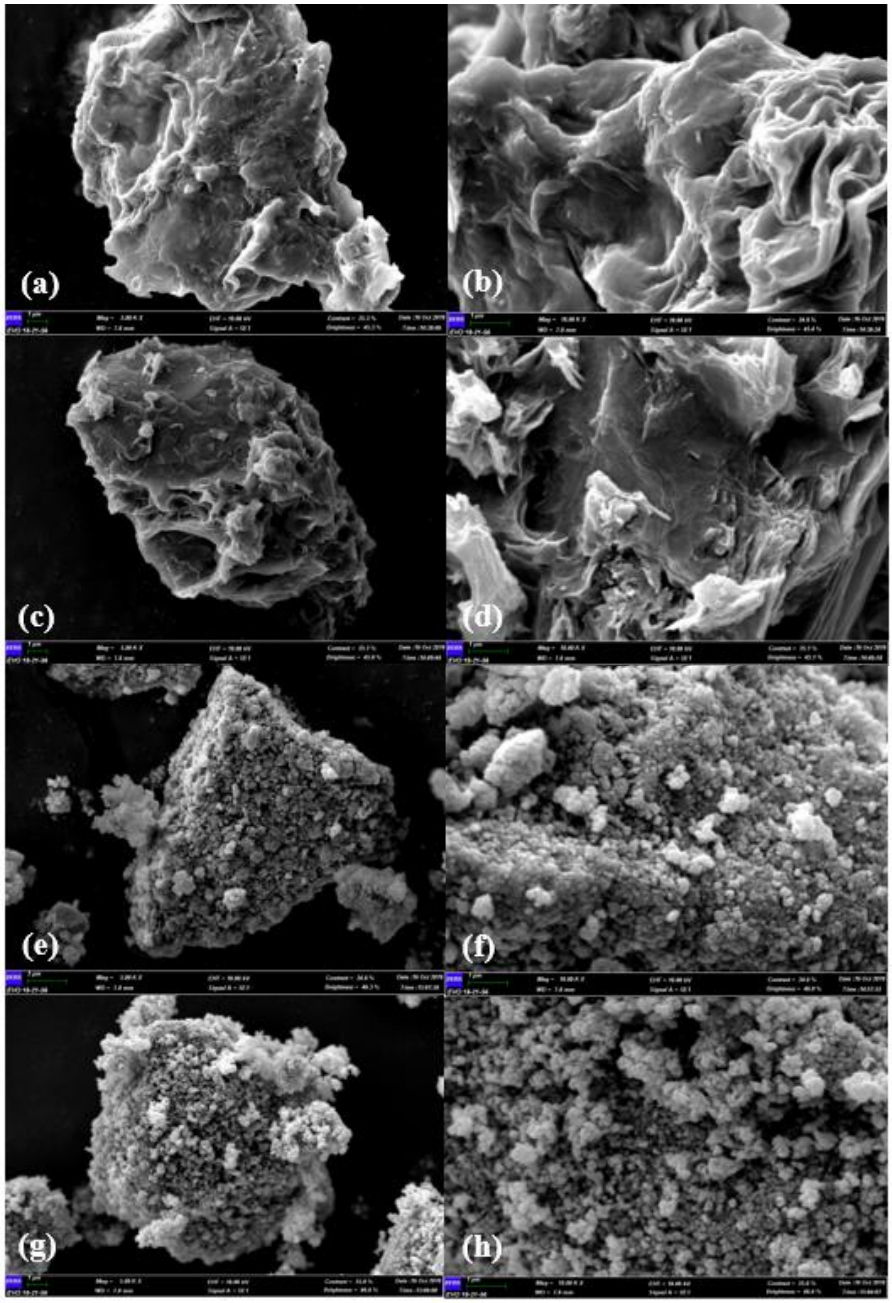


**Figure 5: SEM images at 5000x (left) and 10000x (right) magnification for IZO prepared at various annealing temperatures; (a)-(b) 80°C (as-prepared), (c)-(d) 200°C, (e)-(f) 300°C and (g)-(h) 450°C.**

### *Electrical Conductivity*

The electrical conductivity of IZO with different indium doping concentration is illustrated in Figure 6. The result demonstrates the increase of conductivity of IZO particles with the increase of indium doping percentage. This phenomenon suggests the effectiveness of indium doping as electron donor, as it provides additional free electron resulting from the increased fraction of the interstitial and/or substitution of $In^{3+}$ ions in $Zn^{2+}$ ion sites compared to pristine ZnO. Thus, by increasing the doping concentration, the charge carrier density is increased. Meanwhile, a rise in conductivity is observed at 3% of indium as compared to pristine ZnO,

which is in agreement with other researchers who have claimed a significant increase of charge carrier after 3% of doping concentration [16]. The highest conductivity is recorded at 5% of indium but decrease at 7% of indium doping, probably due to the decrease in crystallite size. As the crystallite size decreases, more grain boundaries will interrupt the electrons movement hence resulted in decrease of conductivity. As the particles was compressed into pallet and then tested for electrical conductivity, it implies how the arrangement of smaller particle size may hinder the electron movement throughout multiple grain barriers.

In addition, the conductivity also shows an increment when annealing temperature is raised. As the annealing temperature increases, more energy is absorbed by electrons, which increases the mobility of conductive charges. Generally, high annealing temperature may produce more oxygen vacancies due to oxygen desorption from the ZnO particles. These oxygen vacancies act as the free carrier (charge carrier) in the ZnO particles, hence improves the electrical conductivity [17, 18]. However, as the annealing temperature is increased up to 450°C, the electrical conductivity is reduced. This finding is in agreement to the result of crystallite size, in which decrease in crystallite size causes an increased electron barriers and electrical resistivity.

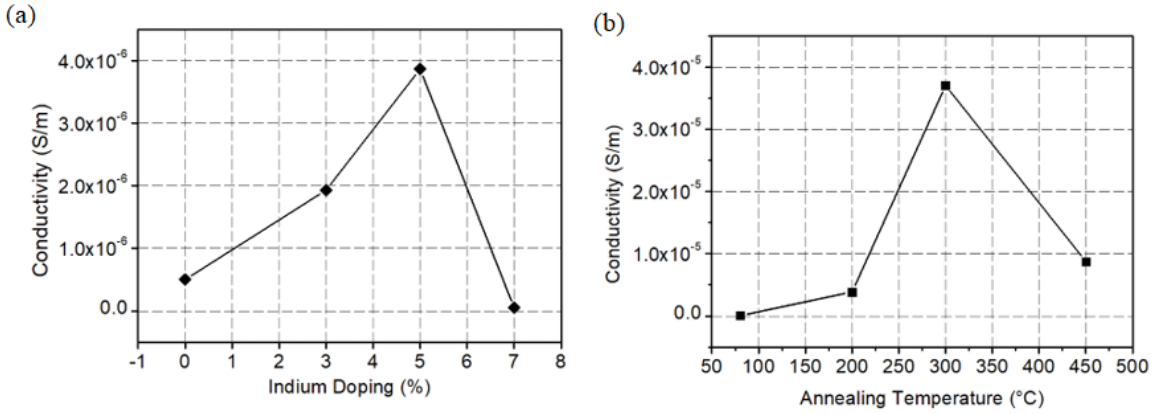


**Figure 6: Electrical conductivity for IZO with (a) different indium doping concentration and (b) different annealing temperature.**

## Conclusion

In this study, IZO powder has been successfully synthesized via low cost sol gel method. The resulted IZO particles produced at different indium doping concentrations and annealing temperatures show distinctive changes in terms of structural, elemental, morphological characteristics and electrical conductivity. It is found that electrical conductivity increases with the increase of indium concentration up to 5% indium, but decreases when indium concentration is further increased which verifies the important role of carrier concentration (indium doping) in increasing the electrical conductivity. A similar result is observed for annealing temperature. The value of electrical conductivity increases as the annealing temperature is increased up to 300°C, but decreases beyond that. The results for conductivity recorded also reflect the results of crystal structure, chemical bonding, microstructure and elemental characteristics of the particles.

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## Author Contributions

All authors contributed toward data analysis, drafting and critically revising the paper and agreed to be accountable for all aspects of the work.

## Disclosure of Conflict of Interest

The authors declare that no known competing financial interests or personal relationships that could have appeared to influence the work reported in the paper.

## Compliance with Ethical Standards

The work is compliant with ethical standards.

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