Effect of egg white as additive for synthesis and characterization of Al doped ZNO nanoparticles by using sol-gel method

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Abstract. Al doped zink oxide nanoparticles were succesfully prepared by simple sol-gel method. Egg albumines were used as the additives. Ethanol was used as the solvent. Zink sulfate heptahydrate and aluminum chloride hexahydrate were used as the precursors with the composition dopant was 7%. The volume variation of albumines were 10, 20 and 30 mL. The nanoparticles were formed by drying at 110°C for 1 hour, after which they were calcined at ± 600°C for 3 hours. The as-prepared Al doped ZnO nanoparticles were characterized by Fourier Transform Infra Red (FTIR), X-Ray Diffraction (XRD) and UV Diffuse Reflectance Spectrometer (UVDRS) and Scanning Electron Microscopy (SEM). FTIR spectra showd that stretching of Zn-O at 441,97-491,58 cm⁻¹ and the stretching of Zn-O-Al at 560,22-570,37 cm⁻¹. The XRD patterns of the ZnO/Al nanoparticles showed that hexagonal wurtzite with the specific peaks at 2θ = 31.6; 34.3; 72; 81 and 90. The sizes of the Al doped ZnO particles produced with 10 mL, 20 mL and 30 mL were 16-80; 14-64; 13-64 nm, respectively. UVDRS analysis showed that the band gap of the ZnO were 2.69; 2.78; and 2.81 Ev for 10 mL, 20 mL, and 30 mL egg white (albumines) respectively. SEM images showed that the nanoparticle produced was spherical with high homogeneity.

1. Introduction
The development of nano-sized crystalline materials (nanotechnology) is a field that has recently become the attention of researchers. Research on nanotechnology can be applied in a variety of applications such as in the medical field, biosensors and and in the industrial field [1].

Nanotechnology research produces nano-sized particles or also known as nanoparticles with a range of sizes around 1-100 nm. Research on nanomaterials has greatly increased in this decade, this is due to the unique physical and chemical properties of nanomaterials. Experimental conditions used in the synthesis or manufacture of nanomaterials play an important role in the particle size of the product produced. Nanomaterials have very many applications. Surface area and unique properties in nano
materials are the main motivations of researchers to develop efficient nanomaterials for renewable energy and clean, oil refinery technology and sustainable environment.

One of the nanoparticles is zinc oxide (ZnO) [2]. ZnO is a class II-VI semiconductor compound that has a hexagonal crystal structure [3]. ZnO has a band gap value of about 3.37 eV and a binding energy of around 60 MeV at room temperature [4]. The properties of ZnO nanoparticles determine their application in various fields so an attempt is made to improve the properties of ZnO. The technique that can be done to improve the optical and electrical properties of ZnO is quite a lot, including through variations in precursor concentration and temperature, addition of surfactants, coatings and doping [5]. ZnO has several advantages such as high transparency in the range of visible light, non-toxicity, environmental friendliness [3] and a relatively inexpensive price [6].

ZnO has a wide application, as can be applied to chemical sensors, transparent conductors, catalysts [7], gas sensors [8], photocatalysis [9], solar cells [10], and light-emitting diodes (LED) [11]. ZnO is a transition metal oxide material that is widely applied as a surface acoustic wave (SAW), ultraviolet (UV) photodiode, spintronic, hybrid solar cell, LED and transparent electrode as an alternative electrode substitute for Indium Thin Oxide (ITO) and FTO. ZnO is also widely applied for gas sensors. ZnO is an important semiconductor oxide that can be used for toxic (toxic) gas sensors and flammable gases. ZnO sensors have several advantages including low price, fast response time, easy to manufacture and small size when compared to other analytic tools.

Some of the methods used to synthesize ZnO nanoparticles are hydrothermal, sol-gel, electrochemical deposition, steam phase process, precipitation. Doping techniques are a common technique to improve the nature and performance of ZnO compounds. Doping with metal elements is also done to improve the optical and electrical properties of ZnO compounds [12], besides that doping can also increase the conductivity of ZnO thin layers [10]. Doping is a technique for modifying the properties of semiconductor oxides. Doping can change the electrical, optical, and magnetic properties of semiconductor compounds.

Doping is carried out by inserting metal elements in semiconductor compounds [13]. Some metal elements commonly used in doping processes are B$^{3+}$, Al$^{3+}$, Ga$^{3+}$, In$^{3+}$ [14], Li$^{2+}$ and Mn$^{2+}$ [15]. Of all n-type dopants in ZnO, Al is very suitable for use as a metal dopant because of its easy availability, ease of doping [16], small ionic radii, relatively cheap compound prices, and Al doped ZnO as well very promising as a high temperature thermoelectric material [17], besides that the substitution of Zn$^{2+}$ ion with Al$^{3+}$ can change the conductivity of ZnO [14].

The method commonly used in the synthesis of ZnO nanoparticles are solvothermal [11], coprecipitation [17], solid state [18], hydrothermal [14], sol gel [19] and [20]. In this study, the sol-gel method is preferred because the sol-gel method has several advantages, namely high product homogeneity, high purity level, relatively low temperature used [19], easily in preparation, low cost, environmentally friendly [2].

Additives can affect the properties of a nanomaterial. Additives can produce high homogeneous and stabilizing material. The addition of these additives can produce products that have a large volume of surface area [21] and [22]. The additive commonly used in synthesizing a ZnO nanoparticle is MEA (Monoethanolamine), but MEA has its disadvantages, which is an expensive price so researchers are interested in finding another alternative, namely egg white. Egg white can be used as an alternative as an additive to replace MEA for synthesis of ZnO nanoparticles because it can be used as a sol stabilizer and facilitates solubility, in addition egg white is an ingredient containing albumin which acts as a bio-template. The advantages including egg whites are easily available and have a much cheaper price.

2. Experimental Section
The equipment used are magnetic stirrer (Brand ATE VELP Scretipica Magnetic Stirr), stirrer bar, glassware, porcelain cup, analytical balance (Precisa XT 220 A), Oven (French Etuves Oven XU 225) and furnace (NEYCRAFT). Oven is used for drying and furnace for calcination. FTIR (PerkliElmer Frontier Optica) is used to view functional groups, XRD (X-Pert Pro) is used to view structures and
purity of crystals, UV-DRS for determining band gap energy and SEM is used to determine the surface morphology of ZnO/Al.

2.1 Materials
All the reagents were analytical reagent grade and were used without further purification. The materials used include: zinc sulfate heptahydrate (Merck), aluminum chloride hexahydrate (Merck), ethanol (Merck), egg white/albumines.

2.2 Synthesis of ZnO/Al Nanoparticle
0.15 M of zinc sulfate heptahydrate was dissolved with ethanol in glass beaker, then continued with stirring process by using the magnetic stirrer at 50 °C for 40 minutes. The dopant source was aluminum chloride hexahydrate with 7% concentration and solution stirred for 40 minutes. The sol mixed with 10 mL egg white/albumines and stirred continue for 60 minutes. The solution is allowed for two nights. The second solution is made by adding 20 mL, and 30 mL egg white/albumines in the same process. The soles of ZnO/Al dried in the oven at 110 °C for 1 hour. The products obtained are calcined in the furnace at 600 °C for 3 hours.

3. Results and Discussion
ZnO/Al Nanocomposite has been synthesized by using Sol-Gel Process. The gel of ZnO/Al shows the the white colour. The albumine with various volumes was added to the solution of zink oxide with vigorous stirred. The variation volume were 10, 20 and 30 mL of albumines. Albumines act as the stabilization agent to change other additives such as monoethanolamine (MEA), diethanolamine (DEA), etc. The composition of dopant was 7% for the synthesis of nanocomposit ZnO/Al. The visual data of ZnO/Al gel can be seen at Table 1.

Table 1. Gel Observation of ZnO/Al nanoparticle

| Samples  | Observation                                      |
|----------|--------------------------------------------------|
| 7%       | The resulting gel is white and the edges are reddish brown (the highest intensity/+++                                 |
| 10 mL    |                                                   |
| 20 mL    | The resulting gel is white and the edges are reddish brown (higher intensity/++)                                   |
| 30 mL    | The resulting gel is white and the edges are reddish brown (high intensity/+)                                       |

3.1 FTIR Analysis
FTIR analysis aims to determine the functional group of ZnO material produced. The range of wave numbers used ranges from 4000-400 cm⁻¹. FTIR will produce absorption peaks that are related to the vibration frequency of the atomic bonds that make up a material. The peak absorption detected is the vibration frequency between the atomic bonds (molecules) that make up a material. Because every different material has a different combination of atomic bonds. Testing of Al³⁺ doped ZnO nanoparticles using FTIR aims to identify the bond between Zn-O and the bond between Zn-O-Al.
FTIR spectra of ZnO/Al nanoparticles with the addition of 10, 20, and 30 mL of egg white/albumine can be seen in Figure 1. There is a widening peak in the range of 680-400 cm\(^{-1}\). This area indicates that in the sample there are Zn-O and Zn-O-Al bonds. This is reinforced by the absorption at 500-400 cm\(^{-1}\) which is the vibration of the ZnO group and the absorption at 594-497 cm\(^{-1}\) shows the vibration of the Zn-O-Al group [23].

### 3.2 XRD Analysis

XRD patterns of ZnO/Al with 10, 20 and 30 mL albumines were obtained at 600 °C for 3 hours. The XRD patterns can be seen in Figure 2, 3 and Figure 4.

The X-ray diffraction pattern of the ZnO/Al nanoparticle prepared by using 10 mL albumines as additive was shown in Fig.2. The XRD pattern of ZnO/Al nanoparticle calcined at 600 °C shows that...
the peak with the highest intensity at 2θ = 34.33, whereas other peaks are at 2θ = 31.19; 31.70; 34.33; 36.16; 36.77; 47.46; 59.32; 62.75; 67.81 and 77.35. The structure of ZnO/Al nanoparticle is hexagonal phase (Wurzite) with ICCD Number 01-076-0704. The average crystalline size of ZnO/Al nanoparticle that prepared with 10 mL albumine was calculated by using Scherrer formula about 16.67-80.38 (Table 2).

Figure 3. XRD pattern of ZnO/Al Nanoparticle with 20 mL albumine

Figure 3 illustrates the X-ray diffraction pattern of the ZnO/Al nanoparticle synthesized by 20 mL albumines as additive. The peaks of ZnO/Al nanoparticles show the peak at 2θ = 31.26; 31.70; 34.35; 36.18; 36.78; 47.46; 55.70; 56.52; 59.41; 62.77; 65.31; 67.82; 69.00 and 77.35. The peak of ZnO was showed of the hexagonal (wurtzite) phase with ICCD Number 01-076-0704. The crystalline size of the prepared ZnO/Al with 20 mL albumines were calculated by using Scherrer formula to be about 14.32-64.30 nm (Table 2).

Figure 4. XRD pattern of ZnO/Al Nanoparticle with 30 mL albumine
The XRD pattern of the ZnO/Al prepared by using 30 mL albumines as additive was shown in Fig. 4. The distinct peaks of ZnO/Al nanoparticle showed at \(2\theta = 31.27; 31.72; 34.35; 36.18; 36.81; 47.47; 56.53; 65.33; 67.87\) and 69.01. The peaks have been classified as peaks of hexagonal ZnO (wurtzite). The standard of ZnO pattern is ICCD Number 01-076-0704. The crystallite size of ZnO/Al nanoparticle was calculated with Scherrer Equation about 13.82-64.30 nm (Table 2).

All the XRD patterns show there is no impurities of the product. All the peak of the ZnO/Al were hexagonal wurtzite. The particle size of the sample was calculated by using The Scherrer Equation.

\[
D = \frac{K\lambda}{\beta \cos \theta}
\]

(1)

where:
- \(D\) is the mean crystallite size of the powder,
- \(\lambda\) is 0.15406 nm is the wavelength of CuK\(\alpha\),
- \(\beta\) is the Full Width at Half Maximum (FWHM) intensity of \(2\theta \times (\pi/180)\),
- \(\theta\) is Bragg’s diffraction angle
- \(K\) is a constant usually equal to 0.89

| No. | Samples                  | Particle size (nm)         |
|-----|--------------------------|----------------------------|
| 1   | ZnO/Al 7% 10 mL albumines | 16.67-80.38                |
| 2   | ZnO/Al 7% 20 mL albumines | 14.32-64.30                |
| 3   | ZnO/Al 7% 30 mL albumines | 13.82-64.30                |

From Table 2, it can be concluded that each sample of Al doped ZnO is a nanoparticle material because it has a particle size ranging from 1-100 nm. This decrease in crystallite value occurs due to differences in the ionic radius of each metal. According to the theory the ionic radius of Zn\(^{2+}\) is 0.74 Å while for Al\(^{3+}\) ion is 0.53 Å. This difference results in different sizes of crystallites. The size of the crystallite formed will be smaller due to the value of the ionic radius of the Al metal which is smaller than the metal Zn. Al doped ZnO has hexagonal wurtzite crystal structure according to ICCD Number 01-076-0704.

### 3.3 UVDRS Analysis

Analysis using UV-DRS was carried out to determine the band gap value of a ZnO nanoparticle. ZnO nanoparticles include semiconductor materials that have two energy bands, namely the valence band and conduction band. Among the valence bands and conduction bands there is a gap called the band gap. Band gap material of ZnO semiconductors has a band gap value of around 3.37 eV [4].

UV-DRS testing is carried out in the range of ultraviolet-visible light, which is in the range of 200 to 800 nm. From this test will be obtained data relation of % reflectance to the wavelength of UV-visible light. The data obtained from this test is processed to obtain an estimate of the band gap energy value of each sample. The band gap energy results obtained from each sample can be seen in Figure 5 and the band gap energy value can be seen in Table 3.
Figure 5. Band Gap Energy Curve of ZnO/Al Nanoparticle with albumine a) 10 mL, b) 20 mL, dan c) 30 mL.

Table 3. Band gap energy of ZnO/Al Nanoparticle with albumines

| No. | Samples                        | Band Gap Energy (eV) |
|-----|--------------------------------|----------------------|
| 1   | ZnO/ Al 7% with 10 mL albumines| 2.69                 |
| 2   | ZnO/ Al 7% with 20 mL albumines| 2.78                 |
| 3   | ZnO/ Al 7% with 30 mL albumines| 2.81                 |

Based on Table 3 it can be seen that the band gap value of ZnO doped with Al ranges from 2.64 to 2.98 eV while the band gap of pure ZnO is 3.37 eV. This is in accordance with the theory which states that the purpose of doping is to reduce the band gap value. The reduced band gap value causes the distance between the conduction band and the valence band to get closer and electron excitation occurs faster, so that the photon energy needed to excite becomes less [24].

3.4 SEM Analysis

SEM analysis aims to determine the surface morphology of ZnO/Al nanoparticles produced. SEM photos of ZnO/Al nanoparticles with Al concentrations of 7% can be seen in Figure 6. The magnification used is 15,000, 30,000 and 50,000 x. From the results of SEM, it can be seen that 7% nanoparticles provide a spherical surface with a uniform particle size distribution (Figure 6). The 7% SEM of ZnO/Al nanoparticles can be seen that the shape is still round (spherical but the distribution of particles is less uniform, whereas the ZnO/Al nanoparticles with 7% Al concentration give spherical surface morphology with a small lump (Figure 6).
4. Conclusion
Nanoparticles of ZnO/Al with albumine were successfully synthesized by sol-gel method. Zink! sulfate heptahydrate and aluminum chloride hexahydrate were used as the precursors. The compositions of dopant was 7%. The XRD patterns of the ZnO/Al nanoparticles showed that hexagonal wurtzite with the specific peaks at 2θ = 31.6; 34.3; 72; 81 and 90. The sizes of the ZnO/Al nanoparticles produced with 10 mL, 20 mL and 30 mL were 16-80; 14-64; 13-64 nm, respectively. The band gap energy of the ZnO prepared with albumines were 2.69; 2.78; and 2.81 eV for 10 mL, 20 mL, and 30 mL egg white (albumines) respectively. SEM images of ZnO/Al nanoparticle showed that the nanoparticle was spherical. Egg white can reduce the particle size of ZnO nanoparticle.

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