Optical and structural studies on bio-synthesized ZnO using *Citrullus lanatus* peel extract

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**Abstract.** Bio-fabrication of ZnO films using plants, enzymes, and microorganisms has been recognized as an environmentally friendly procedure as an alternative to physical and chemical methods. In this research, the optical and structural properties of ZnO thin film have been investigated using UV-Vis spectrophotometer, X-ray diffraction (XRD), and Scanning Electron Microscopy (SEM), respectively. The ZnO films was prepared by spin-coating the mixed solution of Zn(NO₃)₂ and watermelon (*Citrullus lanatus*) peel extract on glass substrate. The ZnO films were then annealed at 400°C for 3h. The UV-Vis absorbance spectra show the strong absorption peaks occurs over a range of wavelengths of 220-380nm, and 190-235 nm for pre-annealed and annealed samples, respectively. The optical band gap of the samples was influenced by the heat treatment. The as-prepared samples synthesized at pH 8 is 3.73 eV and increased up to 5.4 eV after annealed at 400 °C for 3 h. This result suggested that pre-annealed sample has better photocatalytic activity compared to the annealed samples. The XRD pattern of the ZnO films exhibits the ZnO diffraction peaks that correspond to the hkl of hexagonal wurtzite structure. SEM image shows that the morphology of ZnO samples are spherical and rod-like microstructure.

1. **Introduction**

The study to obtain nanoparticles with a unique structure remains a challenge in the field of nanotechnology [1]. The synthesis of ZnO with a unique structure at the nanoscale is expected to be able to increase its activity and physical chemical properties. Biosynthesis or plant-based preparation methods that hold green chemistry principles receive considerable attention regarding the use of materials that are environmentally friendly, non-toxic, and safe during the biosynthetic process [2]. Recently, the use of plant extract-based materials to synthesis ZnO particles can produce unique nanostructure i.e. nanostars, nanorod and nanoflowers [3]. Plant extracts have a dual role in the synthesis process [4]. Plant extract can act as a reducing agent as well as an agent that directs the growth of nanoparticles [5]. Horticultural food waste such as watermelon (*Citrullus lanatus*) rind contains useful biomolecules and compounds that play an active role in reducing metal ion precursors in aqueous solutions to form nanoparticles [6]. Watermelon skin contains flavonoids, glycosids, alkaloids, tannins, saponins, and phenols. The highest watermelon skin contains tannins, alkalids and phenols compared to the pulp and seeds [7]. However, the bio-synthesized ZnO as a thin film is still rarely reported.
In this study, plant extracts will be used as a stabilizing agent as well as a reducing agent in the ZnO synthesis process, namely watermelon rind extract (*citrillus lanatus*). First, the optimum acidity conditions were determined by changing the pH of the synthesis solution, namely 8 and 10. The sample is made in two forms, namely a thin layer and powder so that a very small size is required to increase the surface area. The selected samples were then characterized using UV-Vis, XRD, and SEM.

2. Method
The ZnO nanoparticles were prepared by reacting the precursor solution of zinc nitrate hexahydrate (Zn(NO_3)_2) with watermelon peel extract. First of all, the zinc oxide solution was prepared by dissolving 5 grams of precursor Zinc Nitrate Hexahydrate (Zn(NO_3)_2) in 50 ml aqua DM. Zinc Nitrate solution is added to 50 mL of watermelon rind extract (0.1gr/ml). This condition is made in two pH variations, namely 8 and 10 by adding 5 M NaOH until the desired pH is reached. The solution was then stirred and heated using a magnetic stirrer at a temperature of 80° C until the volume became 10 ml. Plant extracts reacted with Zn^{2+} can reduce the volume of the precursor solution [8]. Samples were made in two forms, namely in the form of powder (S8, S10) and thin layers (TF8, TF10). The powder was taken by centrifuging the solution at a speed of 3000 rpm for 10 minutes. Meanwhile, a thin layer is made by dropping the solution onto a glass slide and then being spin-coated at a rate of 3000 rpm for 30 seconds. The powder and thin layers of the ZnO nanoparticles were prepared in 2 different treatments. The annealing process was not carried out for ZnO nanoparticle powder while the thin layer of ZnO nanoparticles was annealed at 400° C for 3 hours.

The absorbance level of ZnO nanoparticle samples were determined using UV-VIS Spectrophotometer thermo genys 10S. For powder sample, 0.1 mg of sample was dissolved in 3ml DI-water by sonication and put into a cuvette. The UV-Vis characterization was carried out at a wavelength of 300-700 nm. X-Ray Diffraction aims to see the lattice parameters, the crystal structure of the ZnO nanoparticles and to identify the crystalline phases of the ZnO nanoparticle samples that have been synthesized. ZnO nanoparticles in the form of thin films were placed on the sample holder on the diffractometer and then irradiated with a CuKa x-rays at a wavelength of 1.54056 Å. The results of XRD was then processed using the Match 3.0 software application which aims to confirm the phases formed in the ZnO nanoparticles. The surface morphology of ZnO nanoparticles was collected using Scanning Electron Microscopy (SEM) merk FEI, type: Inspect-S50.

3. Result and Discussion
The effect of pH on the ZnO synthesis process was studied using a UV-Vis spectrophotometer. Figure 1 shows the absorbance spectra of the S8 and S10 powder samples after synthesis. The S8 and S10 samples produced ZnO powder as evidenced by the presence of a white precipitate. Based on the results of UV-Vis absorption measurements, the S8 and S10 samples showed high absorption in the 220-380 nm wavelength range.

The results of the UV-Vis absorption spectrum of the annealed thin film samples provided at pH 8 and 10 are shown in Figure 2. After annealing at 400° C for 3 hours the sample showed different results from the non annealed powder sample. UV-Vis absorption is narrowing in the range 190-240 nm. This was probably due to too few samples when characterized. The determination of the energy gap is determined using a Tauc plot of the absorbance data of each sample [9].
Figure 1. Absorbance spectrum of ZnO powder before annealing

Figure 2. The absorbance spectrum of the ZnO thin film after anealling
Figure 3. The plot of \((\alpha hv)^2\) vs photon energy \((hv)\) of ZnO pre-annealing powder samples (a) S8 and (b) S10

Figure 4. The plot of \((\alpha hv)^2\) vs photon energy \((hv)\) of ZnO annealed thin film samples (a) TF8 and (b) TF10

The results of determining the energy gap for each sample are shown in Table 1.

| No | Sample | Energy Gap (eV) |
|----|--------|----------------|
| 1  | S8     | 2.40           |
| 2  | S10    | 3.11           |
| 3  | TF8    | 5.61           |
| 4  | TF10   | 5.48           |

The change in the value of the gap energy in the sample after anneal is thought to be due to the enlargement of the grain. This result is clarified by analyzing the crystal structure of ZnO powder using XRD as shown in Figures 5 and 6.
Figure 5. X-ray diffraction pattern of synthesized powder samples with pH 8 and 10.

Figure 6. X-ray diffraction pattern of thin film samples synthesized with pH 8 and 10 and annealed at 400° C

The results obtained from the XRD characterization in the Figure 6 above show the ZnO phase at the diffraction angle of 31.64°; 34.26°; 36.12°; 47.36°; 56.44°; 62.70° and 67.82° with the hkl (100), (002), (101), (102), (110), (103), and (112). The diffraction peaks obtained correspond to JCPDS data no. 36-1451 which shows that the ZnO phase has a hexagonal wurtzite structure [10]. The diffraction peaks obtained are the same as the results of previous studies [11]. Samples after annealing have a higher intensity than samples before annealing. This happens because in the annealing process the formation of ZnO nanoparticles occurs. The powder samples showed other peaks besides ZnO. This happens when the diffractometer used (sample holder) assumes the X-ray shot produced by the anode. The morphology of the sample was also analyzed based on the SEM characterization results to determine the shape of the ZnO nanoparticles obtained.
The morphology of watermelon rind extract samples synthesized with Zn(NO$_3$)$_2$ precursor with magnifications of 30,000 and 70,000 times is shown in Figure 7. SEM images show that the morphology of ZnO samples is spherical and micro like rods. The observed particle size distribution of the S8 sample was smaller than that of the S10 sample. The concentration of watermelon peel extract in the synthesis process of ZnO nanoparticles also acts as a reducing agent and capping agent to produce nearly homogeneous particle size and morphology [12]. The resulting ZnO nanoparticles size can be measured using the ImageJ application. This application measures the average size of the ZnO nanoparticles by adjusting the scale obtained in SEM characterization. After that, the diameter of the sample is measured according to a predetermined scale. Table 2 shows the sizes of the ZnO nanoparticles. The size of the nanoparticles obtained is still too large because of the size of 100 nm, which is 130.24 nm.

**Table 2.** Particle size comparison of watermelon skin extract solution and Zn(NO$_3$)$_2$ solution

| Sample | Particle Size (nm) |
|--------|--------------------|
| S8     | 117 ± 27.65        |
| S10    | 129.15 ± 24.34     |
4. Conclusion
Biosynthesis or plant-based preparation methods that embrace green chemistry principles receive considerable attention regarding the use of environmentally friendly, non-toxic, and safe materials during the biosynthetic process. The UV-Vis absorbance spectrum shows strong absorption peaks occurring in the wavelength range of 220-380 nm for the annealed samples and 190-235 nm for the pre-annealed samples. The optical band gap of the sample is affected by heat treatment. The prepared sample which was synthesized at pH 8 was 3.73 eV and increased to 5.4 eV after annealing at 400 °C for 3 hours. These results indicate that the annealed sample has better photocatalytic activity compared to the un-annealed sample.

The XRD pattern of the ZnO film shows the diffraction peaks of ZnO which correspond to the hkl hexagonal wurtzite structure. SEM images show that the morphology of ZnO samples is spherical and micro like rods.

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