Effect of pH on the Morphology and Microstructure of ZnO synthesized using Ananas comosus Peel Extract

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Abstract. This research investigated the effect of synthesis pH on the microstructure and morphology of the zinc oxide (ZnO) particles prepared using pineapple (Ananas comosus) peel extract. In this study, ZnO powder were synthesized at different pH, i.e. 8, 9, 10, 11, and 12. ZnO samples were characterized using UV-Vis spectroscopy, Fourier Transform InfraRed spectroscopy, scanning electron microscopy (SEM), and X-ray diffraction (XRD). The UV-Vis absorbances spectroscopy shows the optical absorption peak of the ZnO sample occurred in a wavelength range of 300-360 nm, with bandgap energy of ~3.22 eV. The FT-IR spectrum shows the peak of Zn-O absorption at the wavenumber of 437.55 cm⁻¹ and the reduction of aromatic compounds with increasing of pH. The micrograph of ZnO particles synthesized at different pH shows that the pH affected the size and shape of ZnO. Micro-sized particles with a granular shape have been found at pH 8, and 9, a spherical shape have been found at pH 10, while micro-sized flower-shaped particles have been found at pH 11 and 12. The XRD pattern reveals a wurzite hexagonal ZnO crystal phase with the hkl plane of (101) as the strongest peak, as well as the purity of the sample increasing as the pH value rises. As the conclusion, synthesis pH has a significant impact on the optical, structural, and morphological properties of ZnO biosynthetic powder.

1. Introduction
In recent years, biosynthetic nanoparticles have gained tremendous attention with numerous applications in waste water treatment, food industry and medicine. The biosynthetic method employs materials derived from organisms such as microbes and plant extracts that are environmentally friendly [1]. Biosynthetic techniques provide a way to overcome the drawbacks of physical and chemical synthesis techniques, which use hazardous chemicals, consume a lot of energy, and produce waste that can harm the environment [2]. The use of natural ingredients in synthesizing nanoparticles makes these materials safer to be applied in the fields of agriculture, medicine and the food industry. Those natural ingredients act as a reducing agent, stabilizing agent as well as a capping agent because it contains secondary metabolite organic compounds (phytochemicals) such as flavonoids, alkaloids, tannins and saponins [3].

Zinc oxide (ZnO), II-VI compound n-type semiconductor, has a wide energy band gap of 3.37 eV and a high exciton binding energy of 60 meV at room temperature. Its unique properties and diverse applications in transparent electronics, ultraviolet (UV) light emitters, piezoelectric devices, chemical
sensors, and spintronics have attracted a lot of research attention [4]. ZnO is also categorized as a safe material and has antibacterial properties and has the potential to be used in medicine.

ZnO biosynthesis has been previously reported using extracts of watermelon peel [5], red clover flower [6], alang-alang leaf [7], moringa root [8], and cherry fruit [9]. Pineapple peel contains a lot of antioxidants which are composed of phytochemical compounds. Pineapple peel extract shows potential as a bioreductant, stabilizer and capping agent in the formation of ZnO. The ZnO formation process is influenced by several supply conditions such as temperature, precursor concentration, solvent and acidity level. In this study, ZnO biosynthesis was carried out using pineapple peel extract and Zinc Nitrate Hexahydrate as precursors by varying the pH values of 8, 9, 10, 11 and 12. Optical absorption properties, functional group bonds, morphology and crystal structure of ZnO samples were analyzed based on spectroscopic characterization. UV-Vis, Fourier Transform InfraRed (FT-IR) spectroscopy, scanning electron microscopy (SEM) and X-ray diffraction (XRD).

2. Method

2.1. Preparation of pineapple peel extract
The pineapple fruit peels were removed and thoroughly washed with distilled water, then dried under the sun for a week. The peels were thoroughly crushed in a blender and stored in a sealed container for future use. 5 grams of Ananas comosus peel powder were extracted with 500 mL distilled water and heated for 1 hour at 80°C while stirring using a hot plate. Finally, the extract is filtered using Whatman filter paper no. 1.

2.2. Synthesis of ZnO
1.47 grams of Zinc Nitrate Hexahydrate (Zn(NO$_3$)$_2$.6H$_2$O) was dissolved in Aqua DM and put into a beaker containing pineapple peel extract. In this study, samples were made with varying pH, namely, pH 8, 9, 10, 11, and pH 12. To get the desired pH, NaOH solution was added into the extract solution mixture. The solution was heated at 40°C until a white precipitate is formed. The mixture was then allowed to cool to room temperature and centrifuged at 4000 rpm for 10 minutes. Finally, the ZnO sample was oven-dried at 60°C for a day.

2.3. Characterization
The optical absorption properties of ZnO were characterized using a SHIMADZU UV-Vis spectrophotometer with a wavelength range of 300-800 nm. The functional groups of the sample were detected using SHIMADZU IR Prestige-21 FT-IR spectroscopy. The shape and size of ZnO particles were characterized using Hitachi Flexsem 1000. The structure and crystal size of the samples were studied using an X-ray diffractometer (Rigaku MiniFlex) with CuKα radiation (λ = 0.154 nm).

3. Result and discussion
ZnO powder with various synthetic pH values shows different color for each particular ZnO sample (Figure 1). pH 8 powder is a brownish yellow color. The color of the powder lightens as the pH rises. The brownish yellow color was probably originated from the pineapple peel extract due to low quantity of NaOH as reaction catalyst. The color change from pH 8 to pH 12 also indicates an increasing reduction rate [9]. Meanwhile, at pH 12, the ZnO powder obtained was white, this indicates the higher the purity of ZnO. These results will be explained further in the XRD analysis.
Figure 1. ZnO biosynthetic powder.

Figure 2. (a) The UV-Vis absorption spectrum of the ZnO sample and (b) the bandgap energy curve of the ZnO sample synthesized using pineapple peel extract with varying acidity levels.

The absorption UV-Vis spectrum in Figure 2 of the ZnO sample has a characteristic absorption peak at a wavelength of less than 400 nm. The wide absorption peak at ∼376 nm (∼3.37 eV) is the characteristic peak of ZnO [10]. The pH 8 sample is unique in that there is absorption in the visible light region. This is related to the brownish yellow color of the pH 8 sample from the extract, so it will absorb light in the complementary color spectrum, namely purple-blue (λ = 380-450 nm) [11]. The highest optical absorption value was found in the pH 12 sample and the lowest in the pH 10 sample.

Bandgap energy (Figure 2) was determined from the Tauc Plot method of photon vs (αhν)² energy curves. The bandgap energy value of the ZnO sample obtained is in the range of 3.17-3.23 eV. The difference in the band gap energy value is caused by differences in the particle size of the ZnO sample where the band gap energy will increase as the particle size of the ZnO sample decreases [12].
value of the ZnO band gap energy is reported to vary based on the shape of the particle. Ashar et al [13] reported the band gap energy of ZnO material is 3.21 eV for flower-shaped ZnO and 3.24 eV for pseudo-sphere ZnO obtained from the precipitation method. The difference in the band gap energy value comes from the difference in oxygen vacancy levels in ZnO nanoparticles due to different shapes [14].

Figure 3. FT-IR spectrum of ZnO samples and pineapple peel extract.

The FT-IR characterization aims to determine the functional groups involved in the synthesis and confirm the presence of Zn-O bonds in the sample. The characteristics of the Zn-O bond based on the FT-IR spectrum (Figure 3) are found at the wavenumber of 437.55 cm\(^{-1}\). This position was also found in the biosynthesis of ZnO using pomegranate peel extract [15]. The absorption peak of the Zn-O bond appears to increase with increasing pH value. These results are in accordance with the research conducted by Thi et al (2020) using orange peel extract.

The functional group bonds found at wave numbers 3303.53 cm\(^{-1}\)-3356.97 cm\(^{-1}\), 2335.67 cm\(^{-1}\), 2104.09 cm\(^{-1}\), 1610.27 cm\(^{-1}\), 1562.77 cm\(^{-1}\), 1372.76 cm\(^{-1}\) and 125.20 cm\(^{-1}\) represent the functional groups OH, CN, C≡C, C=C, C=C, CH and CO, respectively. The C≡C functional group at pH 12 looks reduced, while at pH 8 it is still clearly visible. This is thought to be lacking in the addition of NaOH in helping the reduction process so that the pineapple peel extract is still dominant. While the C=C functional group at pH 8 and pH 12 compared to pineapple peel extract shifted to a lower wavenumber. This wave number shift according to Malek and Nahid [9] proves the performance of the reducing agent and the formation of ZnO.

Figure 4 shows the surface morphology (SEM) of ZnO at a magnification of 30,000 times. At each pH value, the particle shape of the ZnO sample changes. Particles were micro-sized, like a ganular, and had indistinct grain boundaries in pH 8 and 9 samples. Meanwhile, pH 10 has micro-sized spherical shape, but it is not uniform. Some of the particles in the pH 11 sample have a micro-sized flower shape, but it is not fully formed. When compared to other samples, the pH 12 particles were in the form of uniform micro-sized flowers with the size (307.6 ± 107.18). The different shape of the particles is due to the increase in the pH value affecting changes in the reaction between H\(^+\) ions and OH\(^-\) ions so that the hydrolysis and condensation processes of particles are not controlled, this causes the formation of interconnected particles and has different shapes [17]. Table 1 shows the average particle size of the ZnO sample. The relationship between acidity level and particle size is in line with the results of research by Ashar et al [13] who reported that changes in size and morphology also affect the band gap energy of ZnO.
Figure 4. SEM photos of ZnO samples with a magnification of 30,000 times.

Table 1. Average sizes of ZnO particles

| Sample | Morphology      | Average sizes (nm) | Photon energy (eV) |
|--------|-----------------|--------------------|-------------------|
| pH 8   | microgranular   | 410,8 ± 157,22     | 3,17              |
| pH 9   | microgranular   | 336,8 ± 153,1      | 3,21              |
| pH 10  | microspherical  | 244,18 ± 136,21    | 3,23              |
| pH 11  | microflowers    | 219,68 ± 72,41     | 3,24              |
| pH 12  | microflowers    | 307,6 ± 107,18     | 3,22              |
Figure 5 shows the X-ray diffraction pattern of the pH 8 and pH 12 samples. The diffraction peak of the pH 12 sample has a higher diffraction intensity than pH 8. This indicates that the pH 12 sample has high crystallinity properties. ZnO diffraction peaks correspond to Crystallography Open Database (COD) No. 96-900-4182 at an angle of 2θ = 31.77°; 34.42°; 36.25°; 47.55°; 56.60°; 62.88°; 67.96°; 72.68° dan76.95° represent the hexagonal wurtzite ZnO crystal planes of (100), (002), (101), (012), (110), (013), (112), (004) and (202) respectively. These results are in line with the research conducted by [16]. The ZnO sample pH 8 exhibits another crystalline phase in addition of ZnO wurtzite phase at diffraction angle of 20,29°; 21,01°; 21,36° dan 27,92°. This is due to the presence of another crystalline phase originated from the pineapple peel extract [18]. It can be concluded that the pH value affects the purity of ZnO, the higher the pH value, the higher the sample purity.

Table 2. Crystal size and lattice parameters of ZnO samples at the highest diffraction peaks (101)

| Sample | 2θ (degree) | Crystal size (nm) | a=b (Å) | d_{hkl} (Å) | c (Å) |
|--------|-------------|-------------------|----------|-------------|-------|
| pH 8  | 36.363      | 15,687            | 3,243    | 2,469       | 5,183 |
| pH 12 | 36,268      | 14,81             | 3,250    | 2,475       | 5,206 |

The crystalline size of the ZnO sample was calculated using the Debye Scherrer equation. The sample at pH 12 had a smaller crystal size than the sample at pH 8 (Table 2). The lattice parameters a and c increased with increasing pH value. The increase in the value of lattice parameters a and c on increasing the pH value with decreasing crystal size occurs due to changes in microstructure, size and shape as well as defects in particles (microstrain) [19]. The lattice parameter values a and c match the lattice parameters of the hexagonal wurtzite ZnO structure with a c/a ratio of 1.6. It can be concluded that the higher the pH of the sample, the smaller the crystal size. These results have also been obtained in a study conducted by Aziz et al [20]. According to Aziz et al [20] different pH values will affect the crystal size, because pH affects the reduction in tensile strain in ZnO with an increase in basicity when the reaction occurs.

4. Conclusions
Biosynthesis of ZnO powder using pineapple peel extract with various pH values has been obtained and analyzed. Increasing the synthetic pH value provides sample with maximum UV-Vis absorption and loss functional groups from pineapple peel extract derived from secondary metabolites. With increasing pH, the morphology of ZnO changes from micro-sized like a granular, micro-sized spherical to micro-sized flowers. Furthermore, increasing the pH results in pure ZnO crystal phase without any other impurities phases. As a result, the optical properties, functional groups, morphology, and structure of ZnO were found to be affected by the synthetic pH.
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