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Biosynthesis of Zinc Oxide Powder Using *Sandoricum koetjape* Peel Extract at Various Annealing Temperature

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Abstract

Zinc oxide (ZnO) synthesized with natural reductants has attracted the attention of researchers because it is environmentally friendly and non-toxic. In this study, ZnO was prepared using S*andoricum koetjape* (*S. koetjape)* peel extract. An aqueous extract of *S. koetjape* peel was used as biological reduction agent for the synthesis of ZnO from zinc nitrate hexahydrate. The ZnO powder obtained was annealed at different temperatures i.e, 300°C, 400°C, and 500°C for 1 hour. Structural, morphological, optical properties, and functional groups of samples were analyzed using X-Ray Diffraction, Scanning Electron Microscopy, UV-Vis Spectroscopy, and Fourier Transform Infrared Spectroscopy, respectively. The X-ray diffraction pattern shows that pure hexagonal wurtzite structure of ZnO particles can be achieved after annealing. The crystal size has also increased with increasing annealing temperature. SEM photo demonstrates the transformation of ZnO particle from spherical to microflower due to annealing. The widest absorption peaks in the UV-Vis spectrum was occurred after annealing at 500°C. The bandgap energy of ZnO increases after annealing from 3.08 eV to 3.20 eV. The FT-IR analysis confirms O-H functional group from extract has been decomposed due to the annealing process. Based on this study, biosynthesized ZnO using *Sandoricum koetjape* peel extract requires annealing process to improve the purity, enhance the light absorbance and change the microstructure of ZnO.

Keywords: ZnO, *Sandoricum koetjape*, reductant, annealing, spherical

1. Introduction

Zinc oxide (ZnO) is a metal oxide semiconductor that has been widely applied in materials science due to its unique physical, chemical, and biological properties such as wide light absorbance, chemically stable and non-toxic[1]. ZnO has been applied in the field of catalysis for wastewater treatment, cosmetics and antimicrobial additives[2]. However, the synthesis method to produce ZnO still involves many toxic chemicals which pose a threat to human health and the environment[3]. The biosynthesis method has received considerable attention because it is cheap, simple, and does not require dangerous chemicals.

Biosynthesis is a method of material synthesis by utilizing media from biological materials such as microorganisms and plants. When compared to biosynthesis using microorganisms, biosynthesis using plant extracts is simpler. This is because the biosynthetic method with plant extracts does not need to prepare microorganism media or cell culture, which is a fairly complicated process[4]. The plant extracts were used as biostabilizer in the synthesis of ZnO. This role is related to the antioxidant activity of the secondary metabolites contained in plants such as flavonoids, polyphenols, and alkaloids. These compounds can be obtained from various plant parts such as leaves, stems, roots, shoots, flowers, bark, and seeds[5]. Various plant extracts have been widely used in the synthesis of ZnO, such as *Aloe vera*, *Camellian sinensis*, and *Borassur flabellifer* leaves[6]. The *S. koetjape* is a traditional plant that is originated from Southeast Asia including Indonesia. The main by-product of *S. koetjape,* the fruit peel, is high in antioxidants which contains alkaloids, flavonoids, tannins, saponins, glycosides, anthraquinone, glycosides and steroids[7]. Therefore, the extract of *S. koetjape* peel is believed to be used as a stabilizer in the synthesis of ZnO. However, biosynthesis of ZnO based on *S. koetjape* peel extract has not been investigated.

Synthetics condition such as precursor concentration, pH level, plants extract used and annealing temperature may result different physical and chemical properties of the material. In this study, ZnO was synthesized using the fruit peel extract of *S. koetjape* at various annealing

temperature. Structural properties, surface morphology, optical properties and functional groups of ZnO samples synthesized with various annealing temperature were analyzed.

2. Material and Methods

2.1 Materials

The materials used in this study were the peel of *S. koetjape* fruit as a stabilizing agent obtained from traditional markets, Pekanbaru City, and zinc nitrate hexahydrate ($Zn(NO_3)_2.6H_2O$) as a source of Zn purchased from Smart Lab. Sodium hydroxide (NaOH) is purchased from MERCK as catalyst and demineralized-water (aqua DM) was used as the synthesis medium.

2.2 Preparation of *S. koetjape* Peel Extract

The peel of *S. koetjape* was cut into small pieces using a sterile knife, then cleaned with water and dried under the sun until the mass was constant. Dried *S. koetjape* peel was grinded using a blender. 20g/L of *S. koetjape* extract was prepared by dissolving 10 grams of peel powder into 500 ml of aqua DM. Extracts solution were heated at 80°C for 10 minutes to increase polyphenol content[8]. The extract was then filtered using Whatman filter paper No. 1 and stored at 4°C for further use.

2.3 Biosynthesis of Zinc Oxide

160 ml of aqueous Zinc Nitrate Hexahydrate 50mM was added into 40 ml of *S. koetjape* peel extract. NaOH was then dripped into the solution to achieve pH of 12. The solution was then heated at 60°C for 2 hours. Afterward, the solution was allowed to settle overnight. The precipitate was separated using electronic centrifuge Oregon at 4000 rpm for 10 min and washed by Aqua DM several times. The obtained ZnO powder was dried at 60°C for 24 h. The ZnO powder was then annealed at different temperatures i.e, 300°C, 400°C, and 500°C for 1 hour. The schematic of the ZnO synthesis is shown in Figure 1.

2.4 Characterization of Zinc Oxide

The optical properties, structure, morphology and functional groups of ZnO samples were analyzed based on the characterizations using Ultaviolet-Visible spectrophotometer (SHIMATSU) in the range 200-800 nm, X-Ray Diffractometer (Rigaku MiniFlex) with CuKα radiation (λ = 0.154 nm), Scanning Electron Microscopy (Hitachi Flexsem 1000), and a Fourier Transform Infared

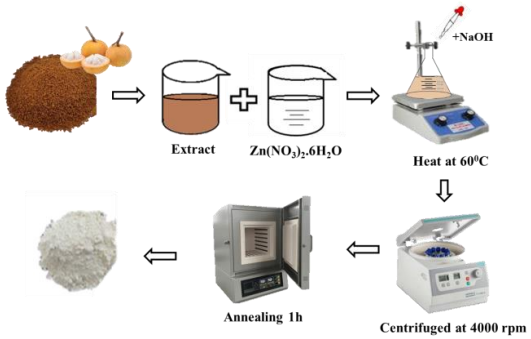

Figure 1. Schematic synthesis of ZnO

spectrophotometer (Simadzu IRPrestige-21), respectively. The particle diameter of the ZnO sample was measured using the ImageJ application by adjusting the scale contained in the SEM image.

3. Result and Dicussion

3.1 Structural Properties

The X-ray diffraction spectrum of the as-prepared (without annealed) and annealed ZnO biosynthetic sample is shown in Figure 2. The diffraction pattern of all ZnO samples exhibits the crystal structure of hexagonal wurtzite ZnO with crystal planes (100), (002), (101), (012), and (110). The peaks of the hkl planes mentioned are the same as the results of previous studies by Sari et al[9].

The ZnO sample with an annealing temperature of 500°C has the highest intensity of the strongest peak which imply its highest crystallity properties. The intensity of the diffraction peak increases as the annealing temperature increases[10]. This indicates an increase in the crystallinity of the sample which is associated with the high thermal energy supplied during the annealing process and promote the

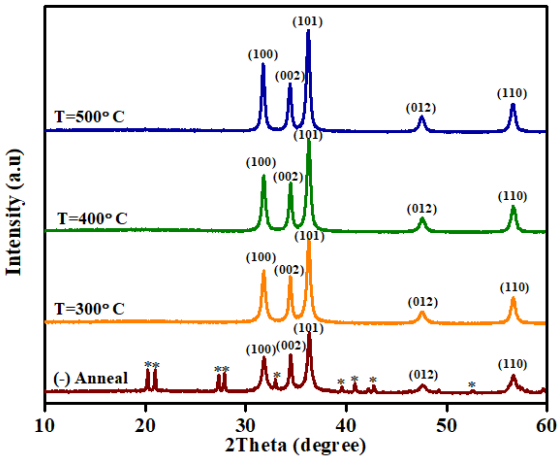

Figure 2. The diffraction spectrum of the ZnO sample without (-) and with annealing

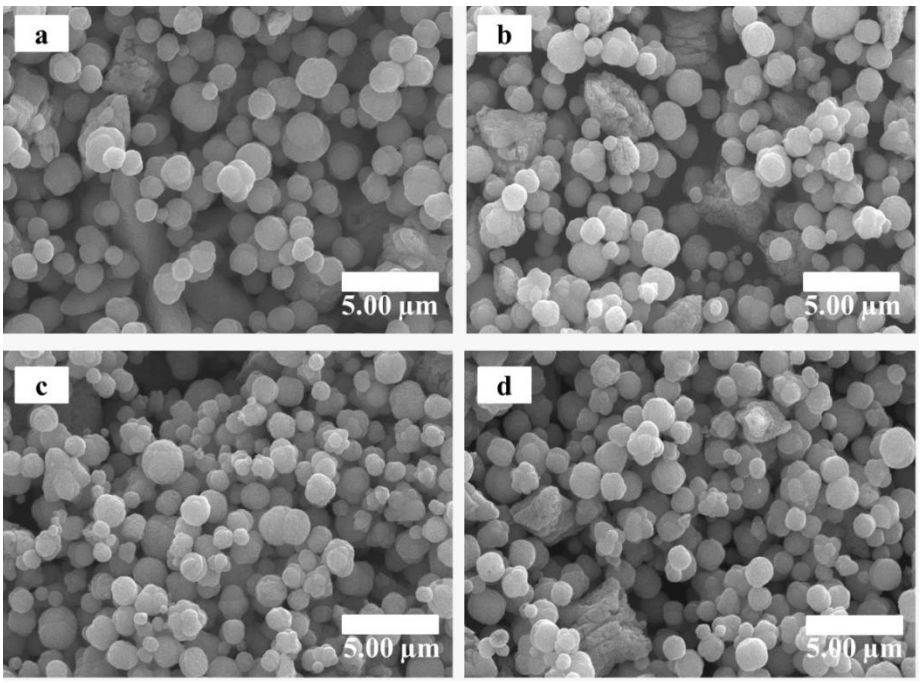

Figure 3. Surface morphology of ZnO samples (a) Without Annealing, (b) Annealing T=300℃, (c) T=400℃, (d) T=500℃ at 10,000X magnification

migration of atoms to the correct lattice position. As a result, crystal defects are reduced and cause recrystallization in the ZnO lattice[11].

In the ZnO sample without annealing, there are another phase indicated by the presence of small peaks (*). This is most probably be due to the influence of the *S. koetjape* peel extract which still existed in the sample. The annealing process can be considered to improve the crystallinity level as well as the purity of the sample. The FWHM value of each sample were obtained by fitting the Gaussian equation and the crystal size was calculated using the Scherrer equation as presented in Table 1.

Table 1. FWHM value and crystal size of ZnO sample at plane (101)

Sample ZnO	2θ (^{0})	FWHM (^{0})	Crystalline Size (nm)
(-) Anneal	36,313	0,444	17,762
300℃	36,263	0,458	17,221
400℃	36,269	0,446	17,684
500℃	36,217	0,428	18,431

The ZnO sample with an annealing temperature of 500℃ had the largest crystal size compared to other samples. This is because the increasing annealing temperature causes the crystal size to enlarge which is indicated by narrowing the FWHM value. This behavior could be attributed to the strain effect or crystallite size increasing that could be contribute to XRD peak broadening[11].

3.2 Surface Morphology

The surface morphology of the ZnO sample synthesis using *S. koetjape* peel extract is shown in Figure 3.

The particle morphology of the ZnO sample is mostly in spherical shape. Particle growth in the annealed ZnO sample is denser than the ZnO sample without annealing. The shape of the annealed sample particles in Figure 3 (b-d) is almost not uniform as evidenced by the presence of flower-like particles. These results are similar to the research conducted by Kabir et al[12].

Table 2. ZnO sample particle sizes

Sample ZnO	Diameter (nm)
(-) Anneal	840 ± 215.7
300℃	839.1 ± 275.2
400℃	794.7 ± 206.1
500℃	750.4 ± 193.4

The size of the ZnO particle diameter is presented in Table 2. Each ZnO sample has only a slight difference in diameter size. Increasing the annealing temperature causes the particle diameter to decrease. The particle size determined based on the XRD results is inconsistent with the results of the SEM analysis. This inconsistency might be due to morphological changing from

spherical to micro-flower shape that occurred during annealing[12].

3.3 Optical Properties

The UV-Vis absorbance spectrum of the synthesized ZnO sample without annealing and after annealing are shown in Figure 4.

Strong absorption peaks of all samples occur at wavelengths around 300-380 nm. The maximum absorption values for each sample are, 0.46 a.u, 1.34 a.u, 0.90 a.u and 1.26 a.u representing samples without annealing, annealed at temperatures of 300℃, 400℃ and 500, respectively. The ZnO sample annealed at 500℃ have a widest absorption peaks. The spectrum obtained is in accordance with the optical properties of ZnO which is generally in the ultraviolet area[13].

The ZnO bandgap energy is obtained from the intersection of the curve $(\alpha h\nu)^2$ versus hν (Figure 5). The band gap energy decreases as the annealing temperature increases. For annealed samples, increasing annealing temperature is followed by a decrease in band gap energy from 3.20 to 3.11 eV which in line with crystallinity improvement as described in the XRD analysis[14].

3.4 Functional Group

The FTIR spectrum of the ZnO sample is shown in Figure 6. Infrared peak absorption for the unannealed and annealed ZnO samples appeared at wavenumbers 443.4 cm^{-1} and 413.6 cm^{-1} are corresponded to Zn-O bond with a hexagonal wurtzite phase[5]. These results are in accordance with the crystal structure analysis using XRD. The annealed ZnO sample has higher Zn-O peak absorption compare to unannealed

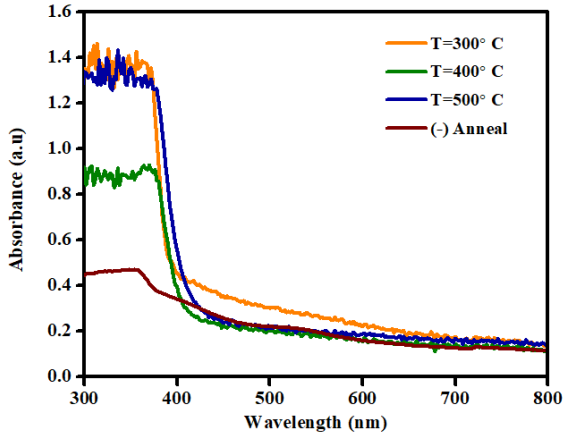

Figure 4. The absorbance spectrum UV-Vis of the sample ZnO

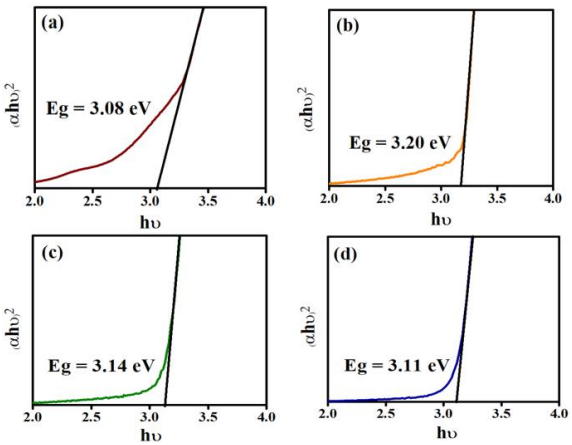

Figure 5. Energy gap of ZnO samples (a) Without Annealing, (b) Annealing T=300℃, (c) T=400℃, (d) T=500℃

sample. It suggests the improvement of ZnO crystalline structure as indicated by the XRD results[15]. The FT-IR spectrum of the green synthesized ZnO NPs also showed phytochemical adsorption on the surface of the nanostructure as stabilizing and capping agents, which strongly protect the nanoparticles from decomposition, deformation, and coagulation processes[16] .

The ZnO sample without annealing has a broad peak at 3237.6 cm^{-1} due to the absorption of the O-H functional group. This bond originates from phenol molecules in the *S. koetjape* peel extract which still attached on ZnO[17,18]. In the 1538.5 cm^{-1} area, the ZnO sample without annealing had a C=C aromatic bond vibration. The absorption peaks at wavenumber ~1290 cm^{-1} for both samples indicate C-N functional groups of amines and amides. In addition, there are also aromatic bonds originating from the C-H functional group in the wavenumber of 844.4 cm^{-1} and 837.8 cm^{-1} at samples without annealing and

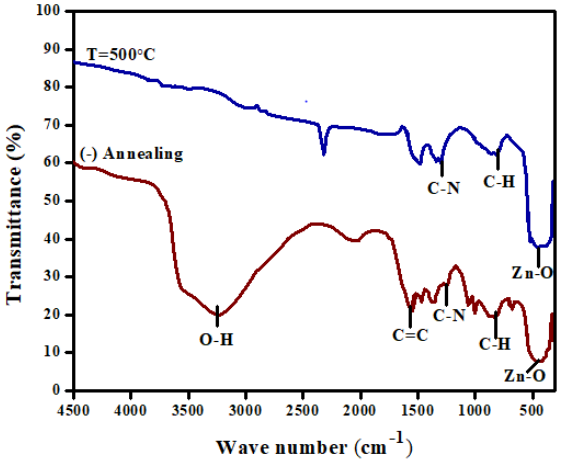

Figure 6. FTIR spectrum of the sample ZnO

annealed samples, respectively. This functional group was also obtained in *Moringa oleifera* extract[18] and *Camellia Sinensis* extract[6]. The transformation of $Zn(NO_3)_2$. $6H_2O$ salt to ZnO nanoparticles are stabilized by O-H functional group from alkaloids, flavonoid, tannin and saponin compounds of *S. koetjape* extract, as also proposed by Martinise et al[18] in ZnO formation with *Moringa oleifera* extract. However, in the sample with an annealing temperature of 500°C, O-H functional group bonds were not found. This is because the O-H functional group has been decomposed due to the annealing process[11,18].

4. Conclusion

ZnO biosynthesis using *S. koetjape* peel extract has been carried out by varying the annealing temperature. UV-Vis absorption of ZnO 500 °C sample shows a widest absorbance at wavelength range of 350-380 nm with a bandgap energy of ~3.11 eV. The XRD pattern shows that ZnO without annealing still contains impurities, while the annealed ZnO is pure a hexagonal wurtzite structure. SEM image indicates few shape transformation from spherical to micro-flower due to annealing. The FTIR spectrum shows the involvement of O-H functional group derived from the peel extract of *S. koetjape* in the process of synthesizing ZnO which acts as a stabilizer and chelating agent. The FTIR spectrum shows the involvement of O-H functional group derived from the peel extract of S. koetjape in the process of synthesizing ZnO which acts as a stabilizer and chelating agent. An annealing step is required for the synthesis of pure ZnO utilizing Sandoricum koetjape peel extract to increase light absorbance, and to modify the microstructure of ZnO.

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