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The Effect of NaOH on the Synthesis of Nano ZnO Using Red Betel Leaves (*Piper crocatum*) by Green Synthesis Method

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Abstract

ZnO has been produced using a green synthesis method. This research aims to determine the effect of NaOH variations on ZnO nanoparticles obtained using red betel leaf extract. The variation of NaOH used is 0,2; 0,4; 0,6; the characterization carried out was Fourier Transformation Infra Red (FTIR), X-Ray Difraction (XRD), Scanning Electron Microscopy (SEM), dan Ultra Violet Vissible (UV DRS) the results of FTIR characterization show that the functional groups in red betel leaves play a role in the information of ZnO nanoparticles, XRD characrerization shows diffraction peaks of ZnO nanoparticles and the presence of $NaNO_3$ phase at 0,2; 0,4; 0,6; and 1 M variation. Then, the SEM results showed a spherical morphology at a 1 M variation, and the UV-DRS results showed an absorption peak at 331 nm and a band gap energy of 3.11 eV.

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Abstrak

Telah dilakuka pembuatan ZnO dengan metode *green synthesis*. Penelitian ini bertujuan untuk mengetahui pengaruh variasi NaOH terhadap nanopartikel ZnO yang diperoleh menggunakan ekstrak daun sirih merah. Variasi NaOH yang digunakan adalah 0,2; 0,4; 0,6; dan 1 M. Karakterisasi yang dilakukan ialah *Fourier Transformation Infra Red* (FTIR), Difraksi Sinar-X (XRD), Scanning Electron Microscopy (SEM) , dan *Ultra Violet Vissible* (UV DRS). Hasil karakterisasi FTIR menunjukkan gugus fungsi pada kandungan daun sirih merah berperan dalam pembentukan nanopartikel ZnO. Karakterisasi XRD menunjukkan puncak difraksi nanopartikel ZnO dan adanya fasa $NaNO_3$ pada variasi 0,2; 0,4; dan 0,6 M. kemudian hasil SEM menunjukkan morfologi berbentuk spherical pada variasi 1 M dan Hasil UV DRS didapatkan puncak serapan 331 nm dan energi celah pita sebesar 3,11 eV .

1. Pendahuluan

Nanotechnology is a technology that involves objects on the nanometer (nm) scale, specifically 1-100 nm. The word nano comes from the Greek "nanos," which means mini size (Lauterwasser, 2006). One of the nanotechnologies that is quite widely known is nanomaterials, which come in various powder types, including nanosilica, nanotitania, nanoalumina, nano-ZnO, and nano-Pb (Zhai et al., 2017).

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There are many ways to produce nano-ZnO, both chemically and physically. These methods include wet chemical, solid-state, precipitation, hydrothermal, and solvothermal methods (Lee et al., 2008). However, physical methods require a significant amount of energy, time, and high temperatures, thereby increasing the environmental temperature. In contrast, chemical methods using reduction agents are harsh and toxic, causing environmental problems (Kawasaki et al., 2006; Pal et al., 2007). Therefore, an environmentally friendly synthesis method is needed.

The green synthesis method is a nanosynthesis technique characterized by a simple, environmentally friendly, and reproducible process (Vinet & Kumar, 2009). The green synthesis method utilizes bacteria, fungi, or plants to synthesize nanoparticles (Pal et al., 2019). Synthesis using plant extracts is faster (Roy and Das, 2015). These

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phytochemical elements include steroids, saponins, carbohydrates, flavonoids, and proteins (Sondi & Salopek, 2004).

Several studies on the synthesis of nano ZnO using the green synthesis method have been conducted, including a study by Suresh et al. (2015) that utilized the Cassia fistula plant and resulted in particles with a size of 5-15 nm. Then, Geetha et al. (2016) utilized the Euphorbia jatropa plant to obtain nanoparticles with an average size of 15 nm.

In this study, red betel leaves were used because they contain a variety of phytochemicals, including glycosides, saponins, flavonoids, alkaloids, essential oils, and tannins (Anggreni et al., 2019). So red betel duan can be used as a capping agent in the synthesis of ZnO nanoparticles.

The size and shape of nano ZnO depend on synthesis parameters, including pH, temperature, NaOH concentration, precursor concentration, and synthesis time. The greater the concentration of precursor or NaOH used, the better the crystals obtained (Singh, 2015). In this research, nano ZnO was synthesized using NaOH concentrations of 0.2, 0.4, 0.6, and 1 M. The aim is to see the formation of particles due to changes in NaOH concentration in the obtained nano ZnO.

2. Research Methods

This research utilized materials such as zinc nitrate hexahydrate (Zn(NO3)2·6H2O) (Sigma-Aldrich), sodium hydroxide (NaOH, 97% purity) (Merck), aquabides, and ethanol. To obtain nano ZnO, several stages were carried out, including the extraction of red betel leaves, synthesis, drying, and characterization using FTIR, XRD, SEM, and UV-Vis DRS.

Extraction is carried out by preparing red betel leaves, then washing them thoroughly with aquabides, cutting them into small pieces, heating them at 100℃ for 5 hours, and grinding them with an electric chopper. After that, boil 20 grams of leaf powder with 100 ml of aquabides for 20 minutes, then filter it with Whatman paper No. 1. This yields the red betel duan extract.

The ZnO synthesis process was carried out by preparing a 0.2 M zinc nitrate solution and then mixing it with 100 mL of leaf extract and 200 mL of zinc nitrate. After that, it was heated to 80℃, cooled to room temperature, and then NaOH was added, with variations as shown in **Table 1**, while stirring with a magnetic stirrer.

Table 1. Variation of NaOH Samples

Samples	Leaf Extract (ml)	Zinc Nitrate 0.2 M (ml)	NaOH (M)
A	100	200	0.2
B	100	200	0.4
C	100	200	0.6
D	100	200	1

After that, it was left for 24 hours, after which the precipitate appeared. It was then separated using a centrifuge. The precipitate was heated at 90℃ until it was dry, and then it was crushed using an agate mortar. The nano ZnO obtained was then characterized using FTIR, XRD, SEM, and UV-Vis DRS.

3. Results and Discussion

FTIR Characterization

Figure 1 shows the FTIR characterization of all samples.

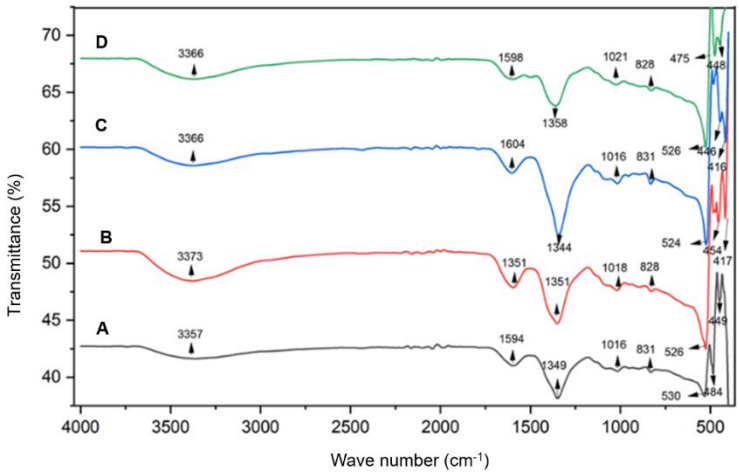

Figure 1. FTIR characterization of nano ZnO

Figure 1 shows the peaks in samples A, B, C, and D at wave numbers 3357, 3373, and 3363 cm^{-1}, which indicate the OH stretching functional group (Song et al., 2009). Next at wave numbers 1594, 1595, and 1598 cm^{-1}, NH functional groups. At wave numbers 1349, 1351, 1244, and 1358 cm^{-1} in the presence of clusters C=O carboxyl function (Vijayankumar et al., 2015), then at wave numbers 1016, 1021, and 1018 cm-1 indicates the presence of

the CN functional group (Kathiveran et al., 2015). Additionally, there are Zn-OH functional groups at wavenumbers 831 and 828 cm^{-1}. The appearance of ZnO functional groups is formed in the wave range of 500-400 cm^{-1}. Functional groups outside of ZnO are thought to be functional groups involved during the synthesis process, which are derivatives of heterocomplex compounds from proteins in red betel leaves (Safitri et al., 2012).

XRD Characterization

XRD characterization was performed to determine the phase and crystal structure of nano-ZnO. The data obtained represents the relationship between intensity and the 2θ angle, presented in the form of a diffractogram, which exhibits diffraction peaks as an expression of the phase and crystal structure.

Figure 2 shows the XRD diffractogram of ZnO synthesis. It can be seen that the XRD pattern obtained corresponds to the hexagonal structure of wutzite with the space group P63MC, as indicated by the standard diffractogram (ICSD 065119, PDF Card No. 01-079-0205) (Albertson, J., Abrahams, S.C., and Kvick, 1989). It can be seen that there are peaks other than ZnO in samples A, B, and C, namely the NaNO3 nitratine peak, as indicated in ICSD 1657009 (Paul et al., 1972). It is estimated that the emergence of the nitratine phase is due to the mixing of zinc nitrate, NaOH, and leaf extract. The chemical reaction of mixing forms the compound NaNO3, also known as sodium nitrate, which then decomposes when the sample is heated. However, in the research carried out, the NaNO3 compound was not completely decomposed, so it remains in the sample, thus affecting the purity of the sample (Yaqin, 2017)

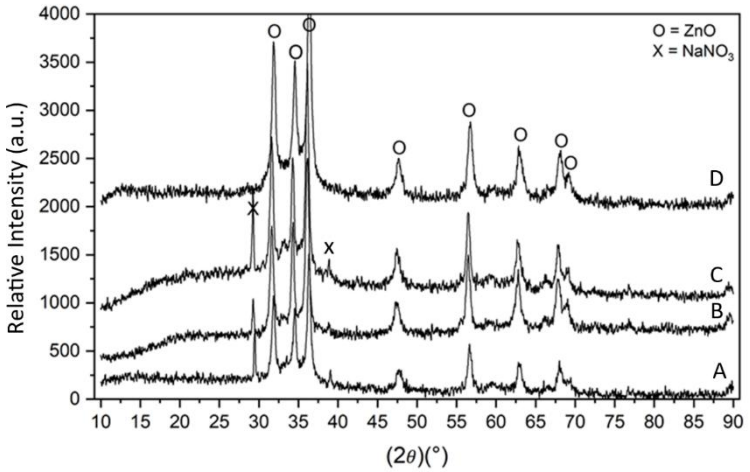

Figure 2. XRD diffractogram of ZnO nanoparticles with NaOH variations (a) 0.2, (b) 0.4, (c) 0.6, (d) 1 M.

From the XRD data, the sample crystal size can be calculated using the Scherrer equation:

$$L = \frac{k\lambda}{\beta cos\theta} \quad (1)$$

Where L is the size of a crystal, B is the peak width at FWHM, and k is a constant with a value of 0.94. The calculation of the size of a particle is presented in **Table 2**.

Table 2. Highest peak angle 2 and ZnO crystal size

Sample	2 Theta (2θ)(°)	*Full Width at Half Maximum* (FWHM) (°)	Crystal size (nm)
A	36.3857	0.3346	21
B	36.1966	0.3011	24
C	36.1377	0.3680	19
D	36.4067	0.4349	16

In general, variations in NaOH do not shift the diffraction peaks; all peaks are consistent at relatively the same angle according to ICSD standards. Based on research by Nurbayasari et al (2017). In general, increasing the molar variation of NaOH does not shift the diffraction peaks; all peaks are consistent at relatively the same angle according to ICSD standards. Variations in NaOH affect the crystallinity of the sample; the greater the concentration of NaOH in the sample, the better the crystals obtained (Singh, 2015). It was explained by Yadav (2018) that increasing concentration is an important factor in the growth of ZnO crystals, as higher Zn^{2+} concentrations experience very fast hydrolysis, resulting in the rapid distribution of Zn^{2+} ions towards the substrate. If intensity is related to the level of crystallinity, as the concentration of NaOH increases, the crystallization level of ZnO also increases. Another interesting aspect of this research is that three samples exhibit a new phase, indicating that the ZnO produced is not pure enough. The phytochemicals in red betel leaf act as a capping agent in the formation of particles and crystals. The phytochemicals contained in red betel include glycosides, saponins, flavonoids, alkaloids, tannins, and essential oil. Based on research by Suresh et al. (2015), the phytochemical content of *Cassia fistula* extract consisted of large amounts of polyphenols and flavonoids. These

two components act as a capping agent in the ZnO nanoparticle synthesis process, successfully synthesizing ZnO nanoparticles with a size of 5-15 nm.

Next, quantitative analysis was carried out by refining the XRD data using the Rietveld method and Rietica software. The crystal model resulting from the refinement uses the Rietveld method with the phase parameters used, namely parameters according to research by Sawada et al (1996) (Sawada et al., 1996) whwew the result $a = b \neq c$ about 3.2523 and 5.2096, also $\alpha = \beta \neq \gamma$ about 90° and 120°, result from refinement values are presented in **Figure 3.**

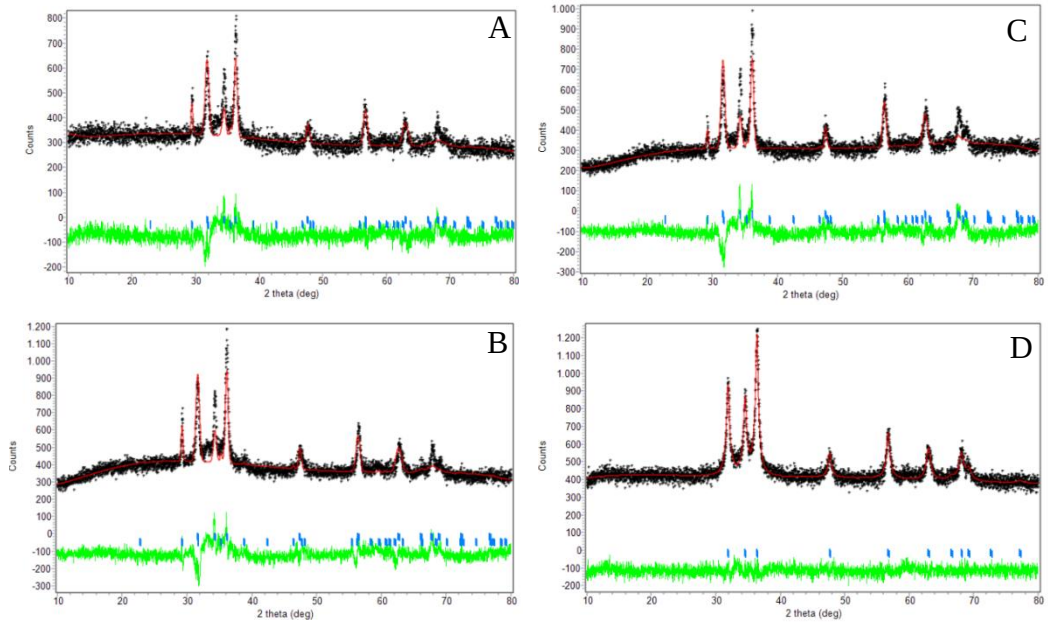

Figure 3. Refine XRD results with NaOH variations (a) 0.2, (b) 0.4, (c) 0.6, and (d) 1 M

After the refinement was carried out, the results of the refinement parameters were obtained in **Table 4**. Research by Kisi (1994) wrote that if the refinement results have a GOF value of less than 4%, the suitability parameters will be met. In this study, the refinement results met the parameter criteria, as explained above, namely *Rp, RWP, Rexp, RB* less than 20% and GOF less than 4%.

Table 4. Results of XRD ZnO data refinement parameters

Sample	R_{WP}	R_p	R_{exp}	*GOF*	R_B
A	7.75	6.03	5.56	1.941	3.20
B	8.86	6.77	5.54	2.312	5.00
C	8.05	6.15	5.03	2.563	3.86
D	5.27	4.16	4.72	1.247	0.02

SEM Characterization

To determine the morphology and particle size of various ZnO samples, it is necessary to use SEM characterization. The results of the analysis using SEM are shown in **Figure 4.**

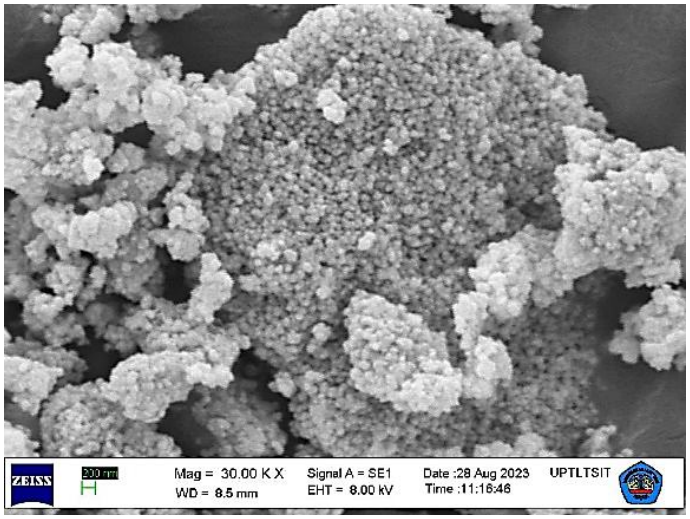

Figure 4. Results of SEM analysis of ZnO samples varying from 1 M NaOH

The results obtained have not succeeded in identifying the size of the ZnO particles because the sample tested is a powder sample. Hence, it has an uneven surface, and the limited Working Distance (WD) capability of the SEM sensor in this case is 8.5 mm. Therefore, if it is forced too close, it will touch the sample and be obscured by the higher part of the sample. Then, the magnification of the SEM tool used reached 30,000 times, producing a less sharp image. However, in Figure 6 at 200 nm, comparison with the SEM image of the sample at a scale of 200 nm shows that the particles already exhibit sizes on the nanometer scale.

The SEM analysis results obtained have a similar shape, which is almost identical to that of research conducted by Geetha et al. (2015), who synthesized nanoparticles using the green synthesis method with the Euphorbia jatropa plant, resulting in a spherical particle shape. So the particle shape obtained from the research carried out had a spherical shape.

UV-Vis DRS Characterization

UV-Vis spectrophotometer is a technique used to evaluate the optical properties of nanomaterials. The optical absorption spectrum of ZnO nanoparticles at room temperature is in the range of 300-800 nm. **Figure 5** shows the spectrum results of ZnO nanoparticles using red betel leaf extract.

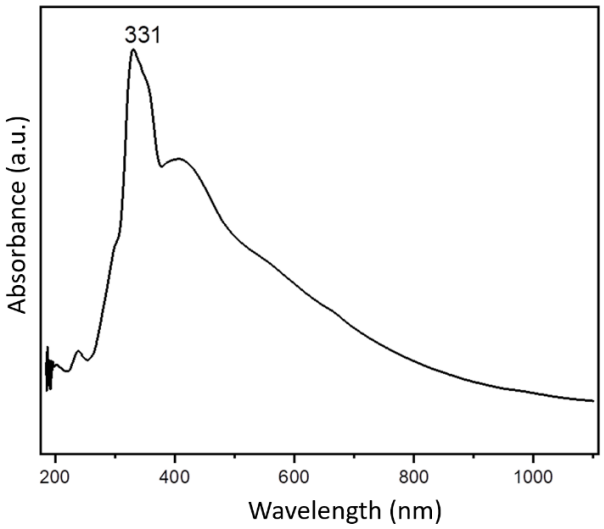

Figure 5. DRS UV-Vis absorption spectrum of ZnO nanoparticles varying from 1 M NaOH

An absorption peak was obtained at a maximum wavelength of 331 nm. This study's results share similarities with those of Geetha et al. (2016), who obtained absorption results in the range of 310-365 nm. Next, the band gap energy of the ZnO nanoparticles obtained from their synthesis was calculated using Equation 2.

$$g = hv = \frac{hc}{\lambda} \quad (2)$$

The band gap energy diagram of the sample with a 1 M NaOH variation is shown in **Figure 6**.

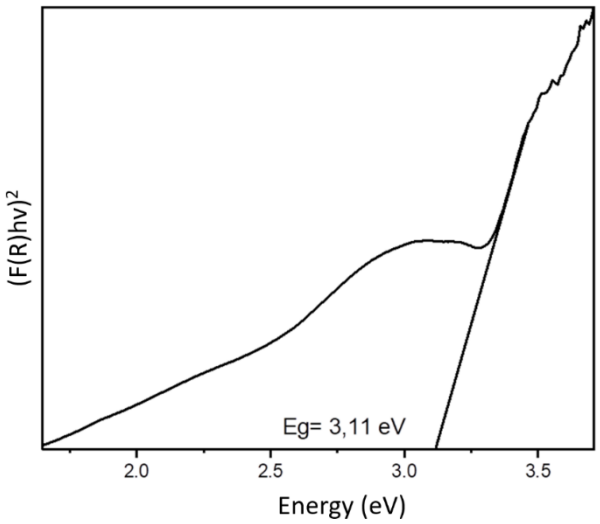

Figure 6 Band gap energy diagram of ZnO nanoparticles varying from 1 M NaOH.

The band gap energy produced in this study was 3.11 eV at a wavelength of 331 nm. The research carried out yields results similar to those of Wirjaksono (2011), which also involved the acquisition of a band gap energy in the range of 3.1–3.2 eV. The magnitude of the band gap energy gain of ZnO nanoparticles can vary depending on the size, morphology, and manufacturing conditions of the ZnO nanoparticles. This change is caused by particle size, which affects the optical and electronic properties of the material when the size is tiny (Geetha et al., 2016).

4. Conclusion

Nano Zinc Oxide (ZnO) has been successfully formed using the green synthesis method with variations in NaOH, resulting in a hexagonal structure. A spherical morphology formed other phases with variations in NaOH concentration of 0.2, 0.4, and 0.6 M, namely the NaNO3 (Nitratine) phase, which is estimated to be due to the calcination process being less than optimal. Identification of functional groups in compounds using FTIR revealed the presence of phenol and polyphenol compounds. In the UV-Vis DRS analysis, a wavelength value of 31 nm was obtained, corresponding to a band gap energy of 3.24 eV. In the analysis using SEM, the resulting image is not satisfactory, making it challenging to observe the specific morphology of the particles.

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