Abstract

The objective of the present work is to develop a procedure for obtaining ZnO nanoparticle via complex formation with plant extracts. *Mimosa pudica* leaves and coffee powder were utilized as template for synthesis of ZnO nanoparticle. After the complex formation, calcination of the complexes at the temperature related to thermal transformation was conducted. DTA-TGA, XRD and DRUV-Vis spectrophotometric analysis were utilized to study the effect of synthesis route to the physicochemical character and methylene blue photooxidation was chosen as reaction model to evaluate the photoactivity. The results show that the materials have crystallite size of around 27.14Å and 46.94Å from the utilization of *Mimosa pudica* and coffee powder extracts respectively. Photocatalytic activity is related to the crystallite size as well as band gap energy values.

Keywords: ZnO; Nanoparticles, Photocatalysis, Green Synthesis.

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1. Introduction

Zinc oxide (ZnO) is a potential photocatalyst instead of TiO$_2$ due to its band gap energy and stability. By its wide bandgap, ZnO can be applied in a broad range of applications, including self-cleaning, photocatalysis and environmental purification. In order to enhance the activity of ZnO in such application in photocatalysis, synthesis of ZnO to form nanoparticles is widely investigated[1].

<table>
<thead>
<tr>
<th>Nomenclature</th>
<th>Description</th>
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<tr>
<td>$\beta_{1/2}$</td>
<td>Full-Width at Height Maximum (FWHM)</td>
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<tr>
<td>$\theta$</td>
<td>Angle</td>
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<tr>
<td>$\lambda_{\text{edge}}$</td>
<td>Edge wavelength</td>
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Several physical and chemical procedures have been reported for the synthesis of ZnO nanoparticles (ZnO NPs) and currently, biosynthesis method is widely utilized. Plant-mediated biological synthesis of nanoparticles is gaining importance due to its simplicity, eco-friendliness and extensive photocatalytic activity[2–5]. Through synthesis by the formation of Zn complex with plant extract, the method is environmental friendly and sustainable. The key active agent in some of these syntheses are believed to be polyphenols, present for example, in coffee, banana peel, and other plant wastes. Greener synthesis of nanoparticles provides advancement over other methods as it is simple, cost-effective, and relatively reproducible and often results in more stable materials[6–8]. The extract of Chenopodium album leaves, mimosa pudica leaves, Aloe vera (Aloe barbadensis Miller) were reported in green synthesis of silver, palladium and other nanoparticles[2,9–12]. From reported results, it is found that the character and size of nanoparticles are depend on the kind of plant extract as well as temperature of oxide formation. Refer to some publications, present work investigates the synthesis of ZnO NPs by comparing the use of two plant extracts; Mimosa pudica leaves extract and coffee powder extract. Study on the thermal transformation of Zn-extract complexes was performed by differential thermal analysis-thermal gravimetric analysis (DTA-TGA). For other physicochemical properties of the NPs x-ray diffraction (XRD), gas sorption analyzer, diffuse reflectance UV-Visible (DRUV-Vis) analysis were studied. Furthermore the photoactivity of ZnO NPs methylene blue photooxidation was chosen.

2. Materials and Methods

2.1. Materials

Materials used in this research consist of zinc acetate dehydrate, methylene blue, isopropanol were purchased from Merk-Millipore. Mimosa pudica leaves was obtained from agricultural area of Ngaglik, Sleman, Yogyakarta, Indonesia.

2.2. Instrumentation

Instruments utilized in this research are DTA-TGA, XRD Rigaku Miniflex 600-Benchtop, UV-Visible Spectrophotometer HITACHI U-2010, and Diffuse Reflectance UV-Visible JASCO.

2.3. Methods:

Leaves extract was prepared by maceration of dry leaves in ethanol solvent overnight followed by filtration and drying to get soft powder. Similar procedure was also applied for coffee extract by using commercial coffee powder. Zn-complexes were synthesize by mixing 20mL of zinc acetate precursor solution and 0.2g of the extract solution in ethanol solvent(20mL) followed by stirring overnight. Furthermore the solvent was evaporated to get the complexes powder designated as Zn-mpl and Zn-cp powders. DTA-TGA analysis was then applied to find the
optimum calcination temperature of each complex. The results from calcination are designated as ZnO(mpl) and ZnO(cp). The samples were analyzed by using XRD, and DRUV-Vis. Photocatalytic activity of materials were tested in MB photooxidation by the addition of H₂O₂ in the reaction system as oxidant.

3. Results and Discussion

Fig. 1 depicts the DTA-TGA thermogram identify the thermal transformation of Zn-complex with plant extract.

![Fig. 1. DTA-TGA Profile of (a) ZnO(mpl) and ZnO(cp)](image)

Weight loss at around 50-100°C is found in both samples indicating the endothermic water removal from the complex. Furthermore the significant weight loss accompanied with exothermic peak are appeared at around 400-450°C. The onset temperature of Zn-mpl complex is at 425°C while for Zn-cp complex is at 450°C. From those onset temperatures the precursor powder of Zn-mpl complex and Zn-cp complex were calcination applied. Thermal transformation is related to the removal of organic compound to form ZnO crystal[13,14]. Both temperatures are pointed out to conduct the calcination of both powder.

XRD pattern of ZnO produced by both plant extracts is presented in Fig. 2. The diffraction peaks from both samples indicate the nanocrystalline formation with identical to the hexagonal phase with Wurtzite structures. The peaks at angles (2θ) around 31°, 35°, 37°, 38°, 56°, 62°, 68°, and 69° correspond to the reflection from 100, 002, 101, 102, 110, 103, 200 to 112 crystal planes, respectively(JCPDS 36-1451). The average crystallite size of ZnO was estimated according to Scherrer’s equation (Scherrer 1918):

\[ d = \frac{0.9 \lambda}{\beta^{1/2} \cos \theta} \]
Where, $d$ is the crystallite size, $\lambda$ the X-ray wavelength (CuKα), $\beta_{1/2}$ the full-width half maximum (FWHM) and $\theta$ is the diffraction angle. It is calculated that crystallite size of ZnO-mpl and ZnO-cp are 27.14 Å and 46.94Å respectively.

The difference in crystallite size is linear to the band gap energy values as recorded by DRUV-Vis analysis which the spectra presented in Fig. 3. By using following formula:

$$E_g = \frac{1240}{\lambda_{edge}}$$  \hspace{1cm} (1)

The band gap energy values of each sample are 2.88eV for ZnO-mpl and 3.10eV for ZnO-cp. The smaller crystallite size of ZnO respects to the higher band gap energy value as a proof of quantum size effect.

Fig.2. XRD pattern of (a) ZnO-mpl and (b) ZnO-cp
Photocatalytic activity of the materials in MB photooxidation is showed by the kinetics of MB reduction over time of treatment in Fig. 4. At the same time, residual MB from photooxidation over ZnO-mpl is higher compared to that of ZnO-cp. The higher concentration means the rate of MB photooxidation conducted by ZnO-mpl is less than that over ZnO-cp and it linearly correlated to the photocatalytic activity of the materials. It is noted that photocatalytic activity seems related strongly to the crystallite size and the band gap energy values.

4. Conclusion

The synthesis of ZnO nanoparticles via complex formation of Zn with Mimosa pudica and coffee powder extracts have been successfully investigated. The XRD spectra indicate that the materials exist in the combination of wurtzite and hexagonal phase with the crystallite size of 27.14Å and 46.94Å respectively. DRUV-Visible analysis reported that band gap energy values of ZnO synthesized from the use of Mimosa pudica and coffee powder are...
2.88eV and 3.10eV. Both crystallite size and band gap energy values are associated with the photocatalytic activity in methylene blue photooxidation.

References


