Synthesis of Zinc Oxide Nanoparticles using Anthocyanin as a Capping Agent

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Abstract: Zinc Oxide nanoparticles have been successfully synthesized by utilizing anthocyanin as a capping agent by thermal decomposition of precursor route. The influence of the high and low concentrations of the anthocyanin to the shape and size of ZnO was investigated in this work. The anthocyanin was obtained from Indonesia black rice extract with methanol as a solvent. The crystallinity and morphology properties were characterized by X-Ray Diffractometer (XRD), and Scanning Electron Microscope (SEM), respectively. XRD result showed that ZnO was formed with good crystallinity without any second phase and had a hexagonal wurtzite crystal structure. SEM result revealed that ZnO with a low concentration of anthocyanin has a spherical shape with a uniform size of about 16 nm while ZnO with a high concentration of anthocyanin has a rod-like shape. The size of spherical ZnO in this work is smaller than ZnO from the same method of synthesis without anthocyanin (~30 nm).

Keywords: Zinc oxide, nanoparticle, anthocyanin, capping agent.

1. Introduction

Zinc oxide (ZnO) is one of n-type semiconductors that has a wide band gap of 3.37 eV and high exciton binding energy of 60 meV at room temperature [1-3]. Moreover, ZnO has some characteristics such as antimicrobial activity, photocatalytic activity, UV absorbance, and piezoelectric that make ZnO can be applied to various applications such as for solar cell, gas sensor, photodiode, photodetector, and anti-bacterial agent [4]. Besides, this material is used in biomedical field because it is non-toxic, biocompatible, and flexible [5].

ZnO has several advantages, i.e. relatively low-temperature synthesis, controllable morphology, and the particular properties that depend on its size [6]. Nano-scaled ZnO has significantly different properties with their bulk. Until this time, there are two kinds of routes utilized to synthesize this material, namely dry process, and wet process. However, the wet processes like hydrothermal, solvothermal and sol-gel are preferable because it is easy to control the parameters and they have relatively low costs. In this route, the activity of controlling the particle size is generally done by controlling the calcination temperature [7]. However, because of their high surface energy, agglomeration frequently occurred [7, 8]. Therefore, it must be restricted by a capping agent. Some works reported the utilization of a chemical-based capping agent to inhibit the growth of nanoparticles
[6]. However, a chemical-based capping agent yields high toxic residual. Therefore, researchers are attracted to use an organic capping agent to replace chemical-based capping agent [9-12] This work reports the use of anthocyanin as a capping agent to fabricate ZnO nanoparticles. The influence of anthocyanin on the morphology of ZnO was also investigated in this study.

2. Experimental Method
The first step of this experiment was the extraction of black rice. The black rice was obtained from Cirebon, West Java, Indonesia. In a typical procedure, black rice was smashed until the soft powder was formed. 100 g black rice was then diluted in 150 ml methanol and stirred for 24 h. The solution was centrifuged to obtain the black rice extracted liquid. Next, 23.7 mmol of Zn(NO$_3$)$_2$ 4H$_2$O was diluted in water and stirred for 30 minutes. 1 ml black rice extract was dropped wisely and stirred at 60 °C until the precipitation was formed. The precipitation was then rinsed with ethanol and deionized water for several times. The result was subsequently calcined at 400 °C for 3h to get white powder.

The synthesis process of ZnO without anthocyanin was performed in the same way without adding the black rice extract. The crystallinity and morphology of ZnO were characterized by X-Ray Diffraction (XRD) and Scanning Electron Microscope (SEM), respectively.

3. Results and discussion

![Diffraction pattern of anthocyanin-capped Zinc Oxide](image)

Figure. 1 Diffraction patterns of anthocyanin-capped Zinc Oxide

The diffraction patterns of anthocyanin-capped ZnO are shown in Figure 1. From the patterns, it can be seen that there was only one phase of the ZnO sample. The sharp peak of the diffraction patterns indicated that the ZnO had excellent crystallinity. In this case, ZnO had hexagonal wurtzite crystal structures with 2θ of 31.775, 34.75, 36.294, 47.498, 56.598, 62.912, 66.379, 67.988, and 69.164. The highest peaks came from the planes of (100), (002), (101), (102), (110), (103), and (113). The data matched the JCPDS card no. 790206. Moreover, there was more than one peak in the patterns indicating that ZnO was polycrystal with more than one orientation. The addition of anthocyanin did not affect the crystallinity of ZnO at all.

Figure 2 (a & b) shows the scanning electron microscopic result of ZnO and anthocyanin-capped ZnO. From the figure, both ZnO and low anthocyanin-capped ZnO had spherical shapes, and the sizes were relatively uniform. The average size of ZnO was measured by Scherrer formula in equation 1,
where $\lambda$ is a wavelength of Cu K$\alpha$ radiation 0.154 nm, $D$ is the size of the crystal, $\beta$ is FWHM, and $K$ is Scherrer constant, in this case, was 0.9. From this formula, the average size of ZnO without anthocyanin was found to be about 30 nm, and the present of anthocyanin could decrease the average size until about 16 nm. Anthocyanin is one of flavonoid substances that can act as a capping agent. Anthocyanin is anthocyanidin with the sugar group mainly consisting of glucoside. Five hydroxyl groups from glucoside and some from anthocyanidin could interact with the surface of ZnO and made the surface passive. They could suppress the growing of ZnO particles during the synthesis and calcination processes. They also could prevent the agglomeration process. Moreover, Figure 2c indicated that a high concentration of anthocyanin could change the shape of ZnO from spherical to rode-like. This phenomenon indicated that the concentration of anthocyanin affected the shapes of ZnO. In high concentration, anthocyanin did not act as a capping agent but as a template for ZnO. The chain of sugar group could serve as a template and make rod-like shaped ZnO. This phenomenon was also observed by other results where glucose or sucrose was used as a capping agent [13,14]. This result is similar to a recent study where the high concentration of glucoside could make rod-like shaped CdO [15].

$$D = \frac{K\lambda}{\beta\cos\theta} \quad (1)$$

Figure. 2 Morphology of ZnO with a spherical shape (a), and low anthocyanin-caped ZnO with a spherical shape (b), and high anthocyanin-caped ZnO with a rod-like shape.

4. Conclusion
The black rice extract or anthocyanin is successfully fabricated and utilized as a capping agent in the synthesis of ZnO nanoparticles. The low concentration of anthocyanin capping agent could decrease the size of ZnO nanoparticles from 30 nm to 16 nm. The high concentration of anthocyanin could
change the shape of ZnO into rod-like. Moreover, the presence of anthocyanin did not affect the crystallinity of ZnO.

5. References
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