

Biosynthesis of ZnO Nanoparticles Using Pumpkin Peel Extract (*Cucurbita moschata*) and its Applications as Semiconductor in Dye Sensitized Solar Cell (DSSC)

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Abstract

ZnO nanoparticles are semiconductor materials that can be used in Dye Sensitized Solar Cells (DSSC). ZnO nanoparticles can be synthesized using pumpkin peel extract (*Cucurbita moschata*) which functions as a reducing agent, stabilizer, and capping agent. Zn(CH₃COO)₂.2H₂O precursor was used with a concentration of 0.15 M at various pH 7, 8, and 9 reacted with pumpkin peel extract. The functional groups of pumpkin peel extract were characterized using Fourier Transform Infrared Spectroscopy (FTIR), the samples were analyzed by TEM and XRD. The resulting ZnO nanoparticles were used as semiconductors in Dye Sensitized Solar Cell (DSSC) using dyes from mangosteen peel. The FTIR results showed the presence of functional groups O-H hydroxy, CH₂, secondary amides (R-CO-NR₂, C-H and phosphate (PO₄³⁻). XRD results showed that ZnO produced wurzhite crystals with a hexagonal system and the smallest crystal size was 18.99 nm. TEM results showed that ZnO synthesized at a concentration of 0.15 M and pH 8 had a spherical particle shape with a size of 24.90 nm, while the DSSC test results had an efficiency of 9.06 x $10^{-4}\%$.

Keywords: Biosynthesis, Cucurbita moschata, dye sensitized solar cell (DSSC), ZnO nanoparticles.

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1. INTRODUCTION

Currently, the use of fossil energy is starting to be minimized, because the supply of fuel reserves tends to decrease. According to the Ministry of Energy and Mineral Resources (2016), Indonesia's oil reserves as of January 1, 2015, decreased by 1.2% compared to the previous year of 3.70 billion barrels. On the other hand, the consumption of petroleum has increased. Based on the outlook of the Ministry of Energy and Mineral Resources in 2016, energy demand in 2015 was 876,594 BOE, it is estimated that the growth of energy demand in 2025 will increase 1.8 times from 2015 and in 2050 it will increase to 5.5 times (ESDM, 2016).

Semiconductor materials with small band gap energy can be utilized in photovoltaic cells such as dye-sensitized solar cells (DSSC). Dye Sensitized Solar Cell is a generation of solar cells with great potential for the future, because DSSC does not require very pure materials so that it can reduce production costs. The potential of solar energy in Indonesia reaches 207.8 Gigawatts, with an average radiation distribution of 4.8 kWh/m2.day (Al Hakim, 2020). The dye used is mangosteen peel extract. (Maulina et al., 2014) stated that the antho-cyanin dye of mangosteen peel (Garcinia Mangostana L) produced a fairly large DSSC efficiency of 0.592%. Abdel-latif et al., (2013) investigate the performance of dye-sensitized solar cells (DSSCs) based on natural dyes extracted from ten different plant seeds.

ZnO can be used as a semiconductor material because it shows good optical and electrical properties so that it has good electronics, potential applications in optoelectronics, and sensors. ZnO as a semiconductor material has high chemical and thermal stability and has a fairly large band gap energy value of 3.37 eV. With this large value, the photon energy charge from sunlight will be absorbed by the DSSC. ZnO nanoparticle synthesis plays a role in reducing the size of the semiconductor in DSSC. The existence of a size effect called the quantum size effect can expand the application of nanomaterials-where the smaller the particle size will increase the energy value of the band gap so that it can increase the efficiency of organic solar cells or DSSC (Gratzel, 2003).

Synthesis of ZnO nanoparticles can be done by physical and chemical methods. Commonly used physical methods include ball mill, laser ablation, and physical vapor deposition (PVD). These methods require quite expensive equipment and produce limited particle sizes and shapes . Commonly used chemical methods include sol-gel, microemulsion and precipitation methods. The sol-gel method is quite good at producing nano-sized particles. Ningsih et al. (2021) synthesized ZnO:Cu by sol-gel methods with different additives (duck egg albumin, monoethanolamine (MEA), and diethanolamine (DEA), where the smallest particles were obtained by adding duck egg albumin with a size of 16.62-53.21 nm. Biological approach through plant extracts as stabilizing agents/surfactants can be used in the synthesis of nanoparticles in order to obtain good characteristics and sizes of nanoparticles. Organisms that play a role in the biosynthetic process include yeast, fungi, bacteria, diatoms, microalgae, cyanobacteria, and plant extracts (Alzahrani, 2015; Parajuli et al., 2020; Mandal et al., 2021).

The biosynthesis of ZnO nanoparticles has been widely carried out. Several successful studies include: 1) Using Sargassum muticum extract that synthesized ZnO nanoparticles in spherical shape with particle size of 30-57 nm (Azizi *et al.*, 2014); 2) Nurbayasari et al. (2017) have succeeded in the biosynthesis of ZnO nanoparticles using Caulerpa sp. with a variation of pH 7,8,9 and a concentration of 0,05;0,10;0,15 M, which obtained the smallest particles at pH 8 and 0.15 M, where the average particle size is 370.72 nm; and 3) Saridewi et al. (2021) also perform at the same variation of pH and concentration, have obtained ZnO nanoparticles from pumpkin seed extract (*Cucurbita moscata*) with a particle size of 28.07 nm at pH 8 and 0,15 M.

In this study, biosynthesis of ZnO nanoparticles was carried out using pumpkin peel extract, where pumpkin peel is an organic waste from pumpkin processing, but still contains metabolites. These metabolites are expected to have functional groups that can act as reducing agents, stabilizers, and capping agents. The resulting ZnO nanoparticles were used as semiconductors in Dye Sensitized Solar Cell (DSSC) using dyes from mangosteen peel.

2. MATERIALS AND METHODS Materials

The materials used in this study were fresh pumpkin peel (*Cucurbita moschata*) and mangosteen peel extract powder obtained from Ciputat, South Tangerang market. Zn(CH₃COO)₂.2H₂O (Merck), NaOH (Merck), ITO glass (Merck), polyethylene glycol (PEG) gel (Merck), CH3COOH (Merck), Triton-X v\(Merck), Whatman No. 41 filter paper (Merck).

Procedures

Simplicia Extract

Fresh pumpkin peel are dried in the sun. Then it is ground using grinding to form a powder. A total of 10 g of dried pumpkin peel powder was placed in a beaker and then added as much as 100 mL of distilled water. Then, a magnetic stirrer was placed in the beaker, and heated in a water bath at 100 °C for 25 minutes while stirring constantly, at a speed of 4000 rpm. The extract was filtered through Whatman No. 41 filter paper. The pumpkin peel extract obtained was divided into three treatments. The first treatment was pumpkin peel extract used for the biosynthesis of ZnO nanoparticles. The second treatment was some samples were stored in a cooler until further use. The third treatment for some samples was they were partially dried using a freeze dryer to be tested for their functional groups using FTIR (Azizi et al., 2014).

Biosynthesis of ZnO Nanoparticles

10 mL of pumpkin peel extract (Curcubita moschata) was reacted with 90 mL of 0.15 M Zn(CH₃COO)₂.2H₂O precursor solution. The mixture was placed in a beaker containing a magnetic stirrer and then heated in a water bath at 70 °C for 1 hour with stirring speed of 4000 rpm. Then, 0.1 M NaOH was added with a mixed pH variation of 7, 8, and 9. The sol-gel product formed was then centrifuged at room temperature of 25 °C at 4000 rpm. The precipitate was taken and washed with distilled water. Then, the solid was dried in an oven at 100 °C. The product was roasted at 100 °C for 18 hours and then calcined in a furnace at 450 °C for 4 hours to obtain pure ZnO nanoparticles (Nurbayasari et al., 2017).

Testing the Efficiency of ZnO Nanoparticle Semiconductor Materials on DSSC

ZnO paste was made by mixing 1 gram of ZnO with 4 mL of acetic acid, stirred for 30 minutes and added by Triton-X, stirred for 30 more minutes. DSSC was assembled first before testing. The ITO glass was cleaned using ethanol and dried at 100°C (15 minutes). The substrate was coated with ZnO paste until evenly distributed. Dry on a hotplate at 30-40°C for 1 hour. The substrate coated with ZnO paste was immersed in a dye solution of mangosteen peel extract for 30 minutes. The ZnO layer was then covered with a carbon resistance electrode (n-electrode) and clamped on both sides with a sandwich structure. Electrolyte coating of polyethylene glycol (PEG) gel was applied between the two electrodes that had been coated with the PEG polymer gel. The efficiency of DSSC performance was tested through current measurement. The series of DSSC measurements are carried out with a potentiometer, multimeter, and sunlight as a light source (Maryani et al., 2012).

3. RESULTS AND DISCUSSION

The FTIR spectrum of Cucurbita moschata pumpkin peel extract showed the main peaks at $3156 \text{ cm}^{-1} - 3302 \text{ cm}^{-1}$, 2931 cm⁻¹, 1560 cm⁻¹, 1393 cm⁻¹, 1036 cm⁻¹. The presence of functional groups at the peak of 3156 cm⁻¹ indicated the presence of O-H functional groups, the range of 3200 cm⁻¹ – 3310 cm⁻¹ indicated the presence of O-H groups on polyphenols or proteins/enzymes or

polysaccharides/carbohydrates. At a peak of 2931 cm⁻¹ indicated the presence of CH₂. At a peak of 1560 cm⁻¹ indicated the presence of a secondary amide (R-CO-N₂). At the peak of 1393 cm⁻¹ indicated the presence of C-H and at the peak of 1036 cm⁻¹ indicated the presence of phosphate (PO₄³⁻) (Skoog *et al.*, 2007). The existence of these functional groups plays a very important role in the nanoparticle synthesis process (Mandal *et al.*, 2021; Parajuli *et al.*, 2020).

Functional groups such as hydroxy (OH) act as stabilizing agents in the biosynthesis of ZnO nanoparticles. According to Chang & Waclawik (2012), this functional group acts as a ligand that donates a pair of electrons to the Zn^{2+} orbital, then Zn^{2+} and the polar group form complex compounds in nanosized templates. Complex compounds are formed by coordinating covalent bonds between ligands and metals. The ligand will donate a pair of electrons to the metal ion providing the vacant orbital. Metal ions act as Lewis acid, while ligands act as Lewis alkaline. The formed complex compound has a more stable chelating effect. ZnO nanoparticles were formed after the calcination process. Functional groups from pumpkin peel assisted with NaOH will reduce Zn^{2+} ions to Zn atoms. Then, the Zn atoms gather and form a Zn cluster. Further growth occurs where the growth rate will affect the particle size. Functional groups from pumpkin peel extract interacted with the Zn compound interface and enveloped the Zn cluster. This event is called 'capping' so that in the formation of ZnO nanoparticles there is no aggregation between nanoparticles and forms stable ZnO nanoparticles. This is due to the repulsion between similar charges caused by the hydroxy group (OH⁻) which plays a role in binding the Zn cluster so that the particle interface is enveloped by negatively charged ions (Nurbayasari et al., 2017; Zobel et al., 2015).

The results of the XRD analysis in Figure 2 showed that all samples had the same diffraction pattern and indicated the presence of a ZnO wurtzite crystal structure with a hexagonal shape. The three variations of pH had a diffraction pattern in the regions of 20: 31.79°; 34,46°; 36.29°; 47.60°;56.66°; 62.95°; 66.45°; 68.02°; and 69.18° with miller index (100) (002) (101) (012), (110), (013), (200), (112), and (201). This is in line with JCPDS no. 9004579 which indicates that biosynthetic ZnO has been formed. The number of H^+ and OH⁻ ions in solution greatly affects the synthesis of ZnO nanoparticles. When the pH is increased and the concentration of OH⁻ ions increases, the density of H^+ ions decreases compared to when the pH is acidic. The presence of OH⁻ ions will affect the crystal structure formed. When the concentration of OH⁻ ions is excessive, it will cause the

hydrolysis and condensation processes during the synthesis of ZnO nanoparticles to become increasingly uncontrollable, resulting in nanoparticles with irregular shapes and sizes (Gontijo *et al.*, 2020; Traiwatcharanon *et al.*, 2017; Yazdani *et al.*, 2021). To determine the effect of increasing the concentration of OH⁻ on the crystallinity of ZnO, pH variations were carried out at 7, 8, and 9.

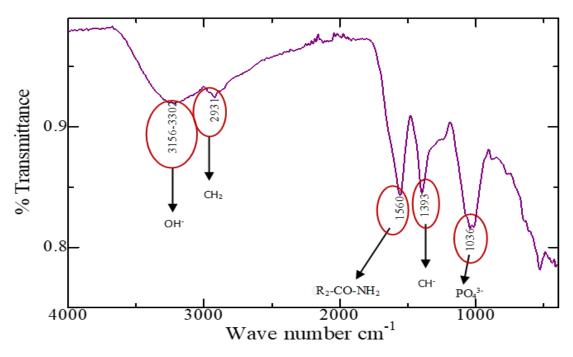


Figure 1. FTIR spectra of pumpkin peel extract

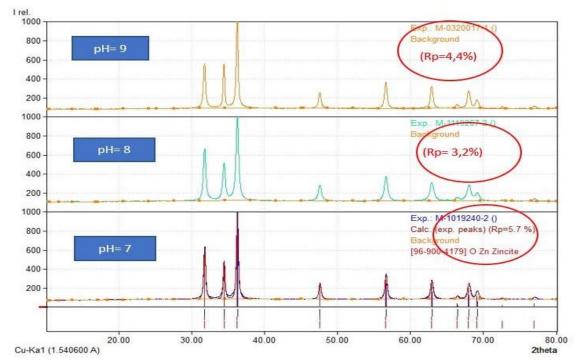


Figure 2. XRD Pattern of ZnO Nanoparticle with various pH

Table 1. Crystal	Sizes and	Crystal	Structures	with
various pH				

Various pH	Crystal Structure	FWHM (°)	Crystal Size (nm)
pH 7	Heksagonal	0.32	26.125
pH 8	Heksagonal	0.44	18.999
pH 9	Heksagonal	0.32	26.123

The smallest crystal size with a value of 18.999 nm was obtained at pH 8 with a of precursor concentration 0.15 Μ $Zn(CH_3COO)_2.2H_2O$ which was the optimal condition for the biosynthesis of ZnO Following Nagarajan nanoparticles. & Kuppusamy (2013) stated that at low pH the aggregation of ZnO nanoparticles leads to the formation of larger nanoparticles around the nucleation. ZnO produced at pH 7 has a larger crystal size of 26.125 nm compared to pH 9 which is 26.123 nm which can be seen in Table 1.

The formation of small crystal sizes was strongly influenced by the addition of NaOH during biosynthesis. The ability of various functional groups to reduce was reduced in the presence of high H^+ concentration at low pH conditions. However, when the pH is increased, the ability of various functional groups as reducing agents increases, thereby increasing stability and preventing agglomeration as the OH⁻ ion increases (Traiwatcharanon *et al.*, 2017).

To determine the level of accuracy or error rate in matching the diffractogram with a reference data, it is necessary to use a quantitative analysis method using the Rietveld method. Refinement of data is carried out in the Match 3 program to obtain an R-profile value (Rp). For samples with a concentration of 0.15 M at pH 7, pH 8 and pH 9, respectively, the Rp. values were 5.6%, 3.2%, and 4.4%. Putra & Priyono (2015) stated that the smaller the value of Rp, the higher the and the better because purity the correspondence between theoretical data and observations is higher. In addition, the smaller the value of Rp, the better the resulting crystallinity. The pH 8 sample shows the smallest value of Rp, which can be seen in Figure 2. This shows that pH 8 is the optimal condition, where ZnO has a smaller crystal size and is purer. Variations in pH did not affect the crystal structure of ZnO. Therefore, electron microscopy characterization and its application to DSSC were only carried out for ZnO at pH 8.

The sample selected is the best sample, i.e. the sample that has the smallest crystal size based on the results of XRD analysis. The sample is 0.15 M Zn(CH₃COO)₂.2H₂O with pH 8. Figure 3 shows the size of the synthesized ZnO nanoparticles that tend to be uniform, the particle size distribution between 12.95 nm - 46.58 nm with an average particle diameter of 24.90 nm. This is due to the presence of protein content in pumpkin peel extract which acts as a stabilizing agent.

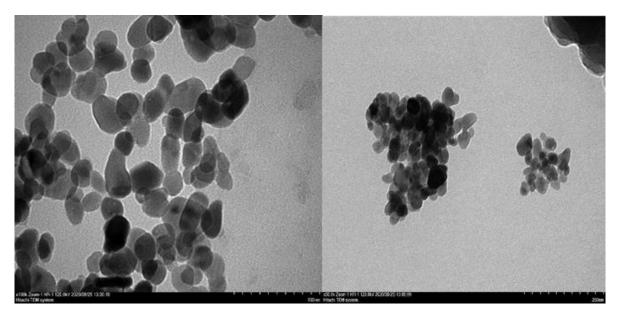


Figure 3. Micrograph TEM of ZnO Nanoparticles

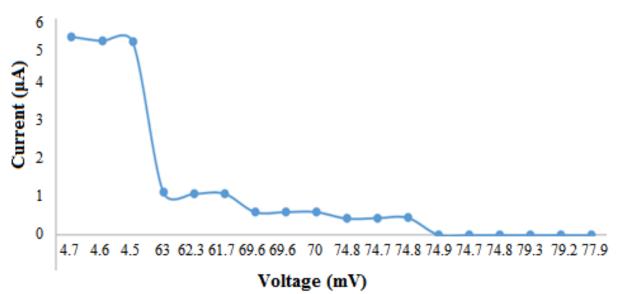


Figure 4. Curve of I-V

By comparing with the results of Nurbayasari et al. (2017) study using Caulerpa sp. that produced ZnO nanoparticles with an average size of 370.72 nm and (Saridewi et al. (2021) using pumpkin seed extract that produced an average size of 28.07 nm, the in this study produced results ZnO nanoparticles with a smaller size of 24.90 nm. The smaller the particle size obtained, the greater the effect that will be generated on the DSSC application. The existence of a size effect called the quantum size effect can expand the application of nanomaterials where the smaller the particle size will increase the band gap energy value so as to increase the efficiency of organic solar cells or DSSC(Gratzel, 2003).

The I-V connection characteristic curve has several parameters such as short circuit current I_{sc} , open circuit voltage V_{oc} , I_{max} or the current that gives the maximum power value, and V_{max} or the voltage that provides maximum power.

In an open circuit (Voc) the solar cell reaches 77.9 mV. The magnitude (Voc) produced by the circuit is still in millivolt (mV) units and short circuit current (Isc) 5.51 μ A. The small current according to Maddu *et al.*, (2007) is due to the resistance of the semiconductor layer and the magnitude of the electrolyte solution. As a result, the electron rate in the semiconductor layer injected from the dye experienced a slowdown. Because the current generated is still small, the maximum power (Pmax) produced is still in milliWatts

(mW) which is 0.01499 x 10^{-6} mW/cm² and fill factor (FF) = 0.1746 with dye immersion time for 24 hours.

The value (FF) corresponds to the formation of a gentle I-V relationship curve. The most ideal I-V curve is a rectangular box shape, although according to Maddu et al., (2007) a very ideal curve is difficult to achieve because of the resistance of the solar cell. The resulting efficiency is 9.06×10^{-4} %. This result is almost the same as Setiawan (2021), where the use of ZnO nanoparticles using pumpkin seed extract with a DSSC efficiency of 9.03 x 10^{-4} %. However, this result is higher than the result of Maryani et al., (2012) were use of ZnO semiconductor synthesized bv coprecipitation method, which is 2.25×10^{-4} %.

4. CONCLUSION

The optimum condition in the biosynthesis of ZnO nanoparticles is the $Zn(CH_3COO)_2.2H_2O$ precursor with pH 8, which produced wurzhite crystals with a hexagonal system and ZnO nanoparticles measuring at 24.90 nm. The efficiency of DSSC produced from ZnO nanoparticles with mangosteen peel dye is 9.06 x 10⁻⁴%.

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