



Synthesis of ZnO Semiconductors By Gel-Combustion with Addition of Citric Acid and Dye Sensitizer

Idawati Supu^{1,*}, Muhlis Ali¹, and Syahdad Aziz¹

Physics Departement, Universitas Negeri Gorontalo, Prof. Ing. BJ Habibie Street, Bone Bolango, Gorontalo, Indonesia, Post Code 96119

*Corresponding author. idawatisupu@ung.ac.id

Abstract. Semiconductor Zinc Oxide (ZnO) nanoparticles was synthesized by method gel-combustion with solubility variations of citric acid (0.2; 0.3; 0.4) mol/L as fuel and calcination temperature at 500°C and 700°C and addition dye sensitizer anthocyanin was extracted from dragon fruit. The composition obtained in the EDS analysis is Zn and O which indicates the formation of ZnO compounds. The surface morphology of ZnO is still agglomerated between particles and has an average size of 816 nm (0.2 mol/L), 555 nm (0.3 mol/L), and 824.5 nm (0.4 mol/L), respectively. The XRD analysis result showed crystal orientation of concentration variation expectively difference, likewise for crystal size distribution and strain orientation was different. The acid citric played important for these case, enhanced concentration caused particle size decreased. The presence of hydroxyl made be weak and polarization ligand bonding in metal-oxygen of Zn-O. The XRD pattern showed diffraction peak a quite similar and wurtzite structure. The result showed lattice strain and crystal size distribution decreased with enhanced addition acid concentration. But the acid 0.3 mol/L presented the smallest crystal size was 27.8 nm. The anthocyanin had given effect not significantly, can be seen in optical result all sample at ultraviolet spectrum region. The absorbance value and wavelength of each sample are different showed absorbance increased with addition citric acid. All samples have the same treatment but the best absorbance and wavelength values at 335 nm, 355 nm and 340 nm, respectively. It obtained sample with 0.3 mol/L very high than another. Furthermore, casting method had to be details in deposition process to produce film which has a wide absorption from UV to visible spectrum region and can be used for solar cell applications dye sensitized solar cell.

Keywords: zinc oxide, gel-combustion, solar cell

1 Introduction

The demands of energy in Indonesia have been significant along with the development of time, resulting in the availability of fossil energy is decreasing [1]. It is predicted that fossil fuels will not be able to supply 46 Tera Watt of energy by the year 2100. In addition, fossil fuels are not considered environmentally friendly because they produce CO₂ emissions, one of the causes of global warming. Moreover, this would need a government policy that leads to renewable energy in reducing CO₂ emissions [2]. For

both reasons, researchers were able to come up with alternative energy sources for renewable and environmentally sustainable energy [3]. In the case of renewable energy, it is most commonly the use of solar energy as one of the main energy sources and is extremely abundant in availability. It was calculated that 0.1% of the earth's surface requires 10% efficient solar cells [4, 5]. Solar energy is one of the active energies that is being developed. One of the utilization of solar energy is to convert light energy into electrical energy by using solar cells [6]. Solar cells are a technological development and have success full fabrication materials divided into three types. In other words, it was the first solar cell made from mono-silicon and polycrystalline silicon. Solar cell was a light harvesting and convert into electrical energy. The first solar cells were made of silicon. Solar cell was a light harvesting and convert into electrical energy. The first solar cells were made of silicon. The second is thin film organic solar cells, and the third is organic solar cells (dye-sensitized solar cells/DSSC). In 1991, Dye-Sensitized Solar Cell (DSSC) was first developed in 1991 by professor Michael Gratzel and is a third generation solar cell used to convert solar One of the advantages of DSSC is that the basic materials used in its manufacture are relatively cheap and environmentally friendly [7]. The conventional solar cells system form were P-N junctions made from semiconductor materials such as silicon use advanced technology but still expensive to develop. Today, semiconductor for solar cell have been efficiency 26.6% by silicon wafer [8]. Until Gratzel discovered dye-sensitized cells from organic materials that were low cost and easy to produce such as extract from plants [9], pigment extract (dye) [10, 11]. The DSSC was one of the potential candidates for next-generation solar cells because they not required materials with high purity values and therefore, have relatively low manufacturing process cost. Contrary to silicon-based solar cells, DSSCs absorb light through dye molecules and separate charges through nanoparticle semiconductor materials with high band gap energy. The band gap energy nanoparticle semiconductor materials like Titanium Dioxide (TiO_2) [12] and Zinc Oxide (ZnO) were highly potential for DSSC application [13, 14]. The band gap energy ZnO similar to TiO_2 and can be an alternative material synthesized easily in various nanostructures [15, 16]. The synthetic or natural dyes can be used as sensitizers. Synthetic dyes generally use ruthenium-based organometallic complexes (efficiency 2.05% and 3.86%) [17, 18], but these synthetic dyes are very expensive. In addition, ruthenium complex-based dyes contain heavy metals that are not very environmentally friendly [19]. Natural dyes are now available from several plants such as leaves, fruits and flowers [20]. Also extracts dye as photosensitizers like chlorophyll, carotene, anthocyanin, curcumin extracts [21, 22]. Semiconductor play an important in charge separation. ZnO used commonly used as great interest as a luminescent nanomaterial, unique property of having a direct band gap groups II-VI, chemical stability, high conductivity, not corrosion [23]. ZnO is known as an environmentally friendly semiconductor with a large band gap (3.3 eV), wide excitation energy (60 MeV), abundance in nature, and natural conductivity [24] and suitable as photo-anode [25]. Developing of nanotechnology era, the synthesis of ZnO metal oxides has been used on a large scale to form nano-scale materials, provided superior electronic and optical properties compared to bulk materials not only related to rod size but also crystallographic orientation [26]. The nano- ZnO synthesis process can be carried out in various ways, including sol gel, auto burning, hydrothermal, electro-

deposition, spray coating, radiofrequency magnetron sputtering, and chemical bath deposition (CBD). Among these methods, the self-combustion method is an attractive option due to its various advantages such as simplicity and low cost. The automated combustion process has advantages such as the ability to control reaction stoichiometry at the molecular level and high uniformity and purity of the synthesized material. The reactivity dissolved process need citric acid (was able to dissolved ZnO 90.4%) [27]. The citric acid as a capping agent in forming nanostructure and crystallinity suitable for utilizing as a semiconductor in DSSCs [28]. The citric acid is a type of acid that has a low molecular weight (0.05 mol/L) capable of dissolving ZnO without polluting the environment [27], because it is unable to biodegrade chemically [29]. The purpose of this research is to make ZnO nanoparticles by gel-combustion method using citric acid as fuel and add with anthocyanin dye. The other purpose of this research is to obtain a new semiconductor material for photo anode solar cells synthesized from dragon fruit dye extract.

2 Method

2.1 Equipments and Materials

The equipment used in the preparation and synthesis of semiconductor materials to dye coating include: a set of Furnace: Notherm furnace tools, glassware, electric heaters, analytical balance (Ohaus Pioneer PX423/E), magnetic stirrer MSH-300i, Scanning Electron Microscopy (SEM) Phenom Pro-X, X-Ray Diffraction (Shimadzu 7000, λ $\text{CuK}\alpha = 1.5405 \text{ \AA}$ with angle $10^\circ \leq 2\theta \leq 90^\circ$ range), and UV-Vis Spectrophotometer (Orion Aqua-Meter 8000).

Table 1. System Precision Data

Sample Name	Element Number	Element Name	Percen Element	Weight Percent	
ZnO (added Citric Acid 0,2 mol/L)	30	Zn	Zinc	33.29	67.09
	8	O	Oxygen	66.71	32.91
ZnO (Citric Acid 0,3 mol/L)	30	Zn	Zinc	36.56	70.20
	8	O	Oxygen	63.44	29.80
ZnO (Citric Acid 0,4 mol/L)	30	Zn	Zinc	71.44	91.09
	8	O	Oxygen	28.56	8.91

The materials used in this study include: zinc acetate dihydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$) p.a Merck product, citric acid ($(\text{C}_6\text{H}_7\text{O}_8) \cdot \text{H}_2\text{O}$) p.a Merck product, preparation glass, PEG 400, ethanol, and dragon fruit.

2.2 Synthesis of ZnO semiconductor nano-materials by Gel-Combustion method

By improving the solubility to 0.3 mol/Liter, zinc acetate dihydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$) as precursor was dissolved in 50 mL of distilled water to generate ZnO solution. The

solution was stirred gently using a magnetic stirrer with a maximum temperature of 175°C at a stirring speed of 350 rpm for 4 hours. During the heating process, citric acid ($C_6H_7O_8$)- H_2O with a solubility variation of 0.2/0.3/0.4 mol/L respectively and then added 1 mL every 20 minutes (up to 10 mL) and play a role as fuel. When the solvent completely evaporates, the solution turns into a gel phase. Then the formed gel phase is put into a porcelain cup and burned using a furnace.

The furnace is set at the initial condition with a maximum temperature of 200°C for 30 minutes where the gel will expand and form like foam. (This situation is called self-propagating combustion reaction to obtain powder material). then the furnace temperature is increased to reach a maximum temperature of 500°C gradually within 3 hours (annealing). When the temperature reaches 500°C, the combustion is stabilized for 1 hour to obtain ZnO with uniform orientation. Then the temperature is increased gradually until it reached 700°C within 3 hours, where sintering conditions will be obtained. The sample can be removed after a while when the furnace is turned off and the temperature is reduced at 100°C from 700°C. The samples were analyzed using SEM and EDS tests.

2.3 Preparation of natural Dye (Anthocyanin)

Dye (Anthocyanin) extracted from red dragon fruit and prepared by cutting into small pieces and mashed then filtered by mesh paper. Extracting of dragon fruit was allowed to marinate in a closed box and rest for 24 hours.

2.4 Deposition of ZnO semiconductor layer on prepared glass by casting method

ZnO semiconductor layer was made by casting method which was deposited on the preparation glass. The preparation glass used was first cleaned with distilled water. A total of 0.017 grams of ZnO semiconductor and 1 mL of PEG 400 were crushed using a mortar and pestle, until a homogeneous paste was obtained. Then, the paste was evenly distributed on the glass plate measuring 1.3×1.8 cm, then heated at 54°C for 10 minutes to remove PEG 400. The sample was analyzed with a UV-Vis spectrophotometer.

ZnO semiconductor layer is deposited using a casting technique on preparat glass, coloured with anthocyanin dye by casting method. First, distilled water was used to clean the preparat glass. A total of 0.017 grams of ZnO semiconductor and 3 drops of dye (anthocyanin) were crushed using a mortar and pestle, until a homogeneous paste was obtained. Next, the paste was evenly distributed on a glass plate measuring 1.3×1.8 cm, then dried. Samples were analyzed with a UV-Vis spectrophotometer.

2.5 SEM characterization and EDS test

Morphological structure analysis was carried out using a Phenom ProX G5 desktop SEM. After the sample is placed on a pin strip secured with sticky carbon tape, it is sprayed to get rid of any light particles that might stick, and then it is coated with the target material—Au/Pd—using a sputter coater. The sample was then coated for 60 seconds at a current of 20 mA. Then the sample was inserted into the SEM using a 12.1 mm distance SE detector with 10kV ETH.

3 Result and Discussion

The ZnO sample that had been imaged at a magnification of 9900x was subjected to a surface morphology study using a scanning electron microscope (SEM) in order to analyse the test findings for surface morphology and energy dispersive X-ray spectroscopy (EDS). Figure 1, the surface morphology of ZnO nano-materials with 0.2 mol/L citric

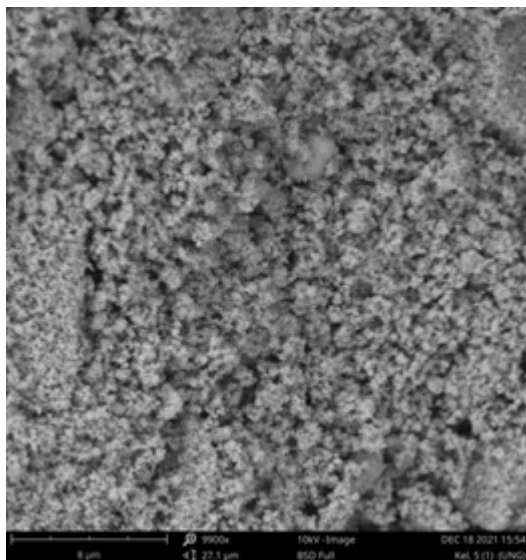


Fig. 1. SEM test results of ZnO powder variation of citric acid solubility 0.2 mol/L

acid solubility was successfully observed. The distribution of particles in this sample looks non-uniform. Analysis of the SEM image showed it contains lumpy particle and spheres, its shape was quasi-spherical [30]. there was agglomeration (clumping) among particles each others caused not uniform shape overall. This sample shows a heterogeneous particle shape with distribution graded size particle average of 816 nm. Figure 2, surface morphology of ZnO nanomaterials with 0.3 mol/L citric acid solubility was successfully observed. The distribution of particles in this sample looks non-uniform, showed spheres that not homogeneous and attached each other and some pores appear on the surface. The particle size distributed heterogeneous as average size 555 nm. Figure 3, surface morphology of ZnO nanomaterials with 0.4 mol/L citric acid solubility was successfully observed. The distribution of particles in this sample looks non-uniform. The sample can be said to still experience agglomeration (clumping) between particles so that the overall shape is not uniform. This sample shows a heterogeneous particle shape with an average particle size of 824.5 nm.

Table 1 shows the EDS analysis results for each ZnO sample with a variation in citric acid solubility of 0.2, 0.3, and 0.4 mol/L. At 0.2 mol/L citric acid solubility, there are weight percent results for the Zn element of 67.09% and the O element of 32.91%.

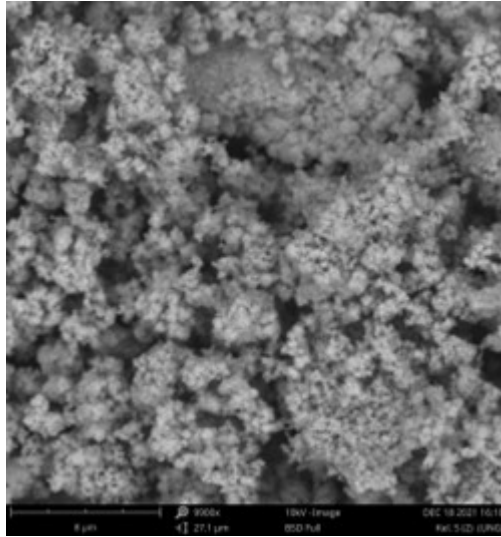


Fig. 2. SEM test results of ZnO powder variation of citric acid solubility 0.3 mol/L

the atomic percent obtained in this sample for the Zn element is 33.29% and the O element is 66.71%. At 0.3 mol/L citric acid solubility, there are weight percent results for the Zn element of 70.20% and the O element of 29.80%. the atomic percent obtained in this sample for the Zn element is 36.56% and the O element is 63.44%. At 0.4 mol/L citric acid solubility, there are weight percent results for the Zn element of 91.09% and the O element of 8.91%. the atomic percent obtained in this sample for the Zn element is 71.44% and the O element is 28.56%. From the whole sample, the presence of Zn and O elements shows the formation of ZnO compounds.

Citric acid has an effect on particle size, the higher the addition of concentration, decreased particle size, but in gradual addition to 0.3 mol/L, the particle size is getting greater than 0.4 mol/L. it had been investigated that the addition of concentration at 0.3 mol/L was greater than the others. Citric acid changed potentially particle size. The surface of ZnO was added with H₂O caused hydroxylation, thus surface was able to adsorb citric acid solution through ligand exchange which results in weak and polarized metal-oxygen bonds, thereby increasing the number of edges, kinks and density defects forming “hot spots” in the solution. This caused the particle size to get smaller [31]. Based on these results, it can be seen that increasing of made particle size be smaller.

3.1 X-Ray Diffraction Analysis Results

Based on Figure 4, the concentration difference of citric acid showed no significant crystallinity pattern, and its nanoparticles have a hexagonal wurtzite structure (JPDS No. 2300112) that corresponds to the *hkl* plane orientation (100), (002), (101), (012), (110), (013), (200), (112), (201), (004), (202), (014), (023). The peak diffraction positions are 31.79°, 34.30°, 36.30°, 47.61°, 56.22°, 62.92°, 66.38°, 67.96°, 69.13°, and

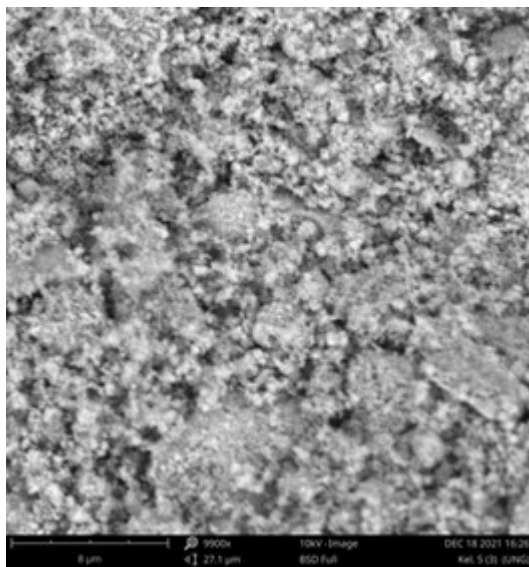


Fig. 3. SEM test results of ZnO powder variation of citric acid solubility 0.4 mol/L

72.62°. The average crystallite size of the prepared samples was calculated using the Debye–Scherrer equation:

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

where $k = 0.9$, λ is the X-ray wavelength (1.54 Å), β is the FWHM, and θ is the Bragg angle. The crystallite sizes at different dissolution concentrations (0.2 mol/L, 0.3 mol/L, and 0.4 mol/L) are calculated as 54.8 nm, 27.8 nm, and 33.2 nm, respectively.

Presenting the diffraction peak's intensity clearly increases when the acid concentration rises from 0.2 mol/L to 0.4 mol/L and indicate wurtzite. As the concentration of citric acid increases, there is a slight rise in the diffraction peak's intensity. Except for the treatment of 0.3 mol/L, the crystal size is the smallest compared to 04 mol/L. In addition, annealing is also very influential on changes in crystallinity, but in this study no variation in annealing temperature was carried out, only the maximum fixed temperature at 700°C all samples. The excess complexing agent quickly accumulates around the zinc ion as citric acid level rises. It combined to generate complex compounds that are too dense for the zinc ion to readily pass through. ZnO crystal reduce in size as a result of the lattice strain growth. The presence of citric acid causes the solution's surface tension to reduce, decreasing the energy needed to create a new phase and permits the formation of ZnO crystals at a lower super-saturation. On the contrary, two chelate rings—a pentabasic ring and a hexahydric ring—are formed by the zinc ion and citric acid [32]. Growing units have an enlarged spatial volume due to the occurrence of the two chelate rings. The complex chemical molecules have a tendency to be perpendicular to the precursors when calcined and the growth units have a tendency to face-land

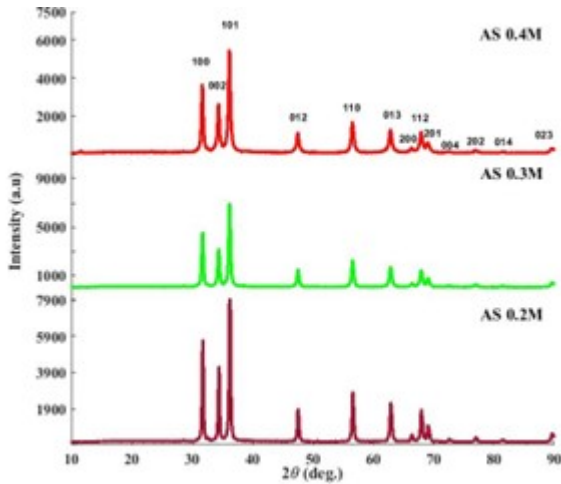


Fig. 4. The results of XRD analysis on each difference in citric acid concentration of 0.2 mol/L, 0.3 mol/L and 0.4 mol/L.

onto the growing interface. Growing units that land on their faces on the axial direction are more energetically preferred than those that land on their edges or vertices along the radial direction, as this type of landing and dehydration will produce three Zn–O–Zn bonds. In this type of face-landing on the [0 0 0 1] crystal face, The [0 0 0 1] direction would be the preferred path for the ZnO crystal plane to grow [32].

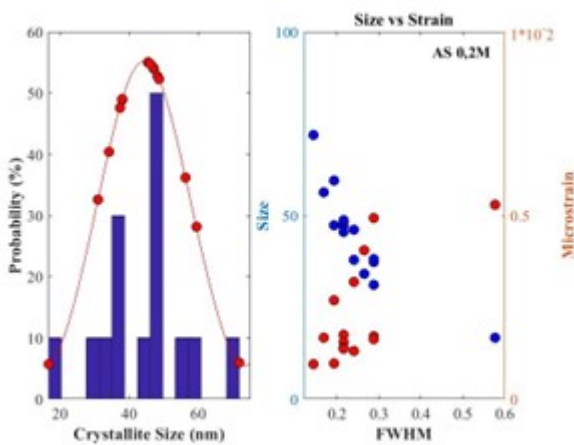


Fig. 5. Size and strain distribution results used citric acid concentration 0.2 mol/L

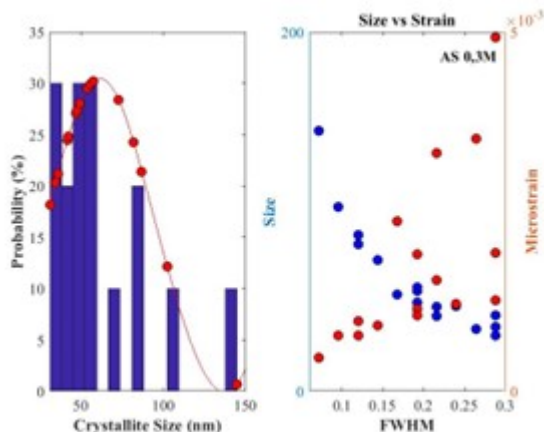


Fig. 6. Size and strain distribution results used citric acid concentration 0.3 mol/L

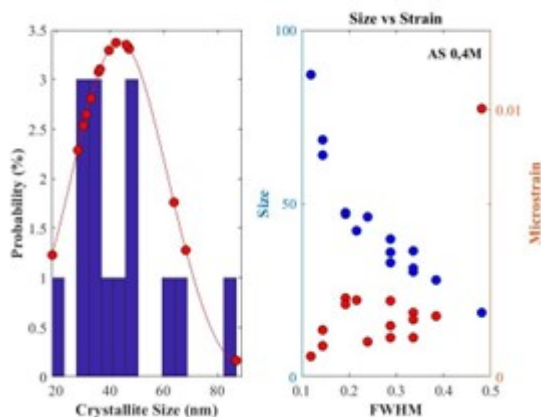


Fig. 7. Size and strain distribution results used citric acid concentration 0.4 mol/L

Lattice strain represents the constant distribution of crystal defects. Figure 5-7 shows the value of lattice strain and crystal size distribution decreases. It can be seen that a decrease in lattice strain from 9.59×10^{-4} to 4.92×10^{-3} with the lowest crystal size distribution at 9.59×10^{-4} to 4.92×10^{-3} and 16.64 nm and 71.89 nm (Figure 5); 4.66×10^{-4} to 4.92×10^{-3} with a crystal size distribution 31.04 nm to 145.10 nm (Figure 6); 7.77×10^{-4} to 1.005×10^{-2} with a crystal size distribution decreasing at 18.43 nm and 87.02 nm, respectively (Figure 6).

This lattice strain decrease indicates a decline in defects in the crystal. The reaction that occurs when citric acid is added has an effect on the crystal size in addition to

the annealing temperature. Because citric acid contains carboxyl and hydroxyl groups which formed two chelate rings that affect the growth rate and crystal orientation. The adsorption of growth units on crystal surfaces has been discovered to substantially influence crystal growth rate and orientation [33].

3.2 The Optical Properties Analysis of ZnO

Figure 8. showed absorbance spectrum of ZnO was added citric acid solubility variations of 0.2/0.3/0.4 mol/L. At 0.2 mol/L citric acid solubility, a peak is obtained at a wavelength of 335 nm with an absorbance of 3.708. Then citric acid solution 0.3 mol/L and 0.4 mol/L, a peak was obtained at a wavelength of 355 nm and 340 nm, absorbance 4.242 and 3.999, respectively.

Wavelength absorption occurs in the ultraviolet (UV) region such as 300 nm-350 nm. The concentration of 0.3 mol/L citric acid has the maximum absorbance value, while the lowest value is 0.2 mol/L. This is because the concentration was more visible and physical, the film thickness was thicker, and there were more atoms present to absorb light beams, due to the influence of citric acid. Acid solution, temperature, and anions all have a significant impact on ZnO dissolution. Citric acid, because it has trichaboxylates, can increase deprotonation to form various complex bonds (consisting of metal ions and molecular bond-forming substances from several ligands) interacting with the zinc surface [34]. In addition, the interaction of ZnO and citric acid is also strongly influenced the presence of other substance [27].

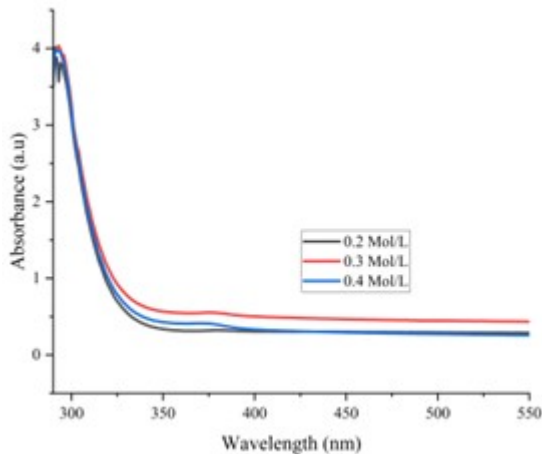


Fig. 8. The absorbance of ZnO with citric acid concentration variation (0.2 mol/L, 0.3 mol/L, and 0.4 mol/L).

Anthocyanin dye extraction was obtained with absorbance absorption at a wavelength of 550 nm with absorbance value 2.864. However there was no difference between ZnO before and after dye addition significantly (Figure 9). there was no shift to

the visible region. This is most likely due to the fact that casting dye coating calls for a more involved process.

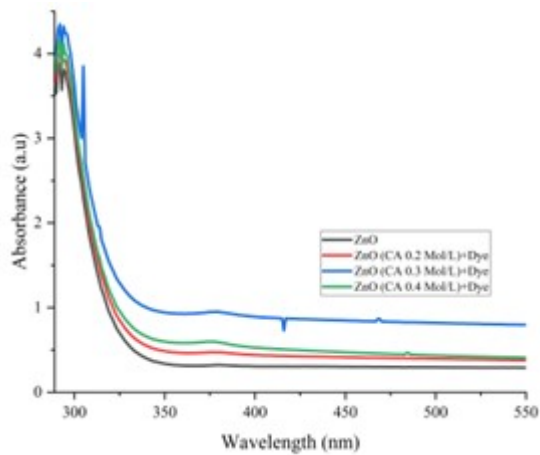


Fig. 9. The absorbance of ZnO with without dye, and ZnO synthesized with dye added citric acid concentration variation (0.2 mol/L, 0.3 mol/L, and 0.4 mol/L).

Figure 9. showed the result of comparison between each sample that has not been coated with dye and samples that have been coated with dye. This graph shows that the dye (anthocyanin) has no effect on any of the samples that have been coated with it. All of the samples' nearly identical absorbance readings and wavelengths serve as proof of this. This is influenced because the samples tested are still in an alkaline state or in other words, the particles in the sample are still not completely fused.

4 Conclusion

ZnO nanomaterials have been successfully synthesized using the gel-combustion method with variations in citric acid dissolution. The variation of acid citric played very important for particle and crystal size formed. The best molarity was showed at 0.3 mol/L and recommended for the next optimisation. This method was influenced by acid addition in ZnO nanoparticle formed. Absorbance also increases along with the enhancement of concentration. The casting method in thin film coating need to be further improved, as well as for antochyanin dye deposition to get maximum result.

References

1. S.M. Siagian, J. Elektro dan Mesin Terap. 7(2), 51 (2021)
2. T. Güney, Renew. Energy **184**, 791 (2022)

3. F.M. Labib, Harjito, S.H. Saputro, Indo. J. Chem. Sci. (Indonesian J. Chem. Sci.) **1**(1), 85 (2012)
4. A.P. Uthirakumar, in *Solar Cells - Dye-Sensitized Devices* (InTech, 2011)
5. Y. Majeed, et al., *Energy Reports* **10**, 344 (2023)
6. R.F. Irnawan, Y. Ismail, J. Innov. Mater. Energy, Sustain. Eng. **1**(2) (2024)
7. M. Grätzel, J. Photochem. Photobiol. C Photochem. Rev. **4**(2), 145 (2003)
8. X. Ru, et al., *Joule* **8**(4), 1092 (2024)
9. I. Afandi, I. Iswadi, A. Aisyah, H. Hernawati, JFT J. Fis. dan Ter. **6**(2), 176 (2019)
10. B. Alkali, J.B. Yerima, A.D. Ahmed, S.C. Ezike, *Optik (Stuttg.)* **270**, 170072 (2022)
11. K. Mensah-Darkwa, F.O. Agyemang, D. Yeboah, S. Akromah, *Mater. Today Proc.* **38**, 514 (2021)
12. G.G. Ninan, M. Varghese, M. Balachandran, *Opt. Mater. (Amst.)* **149**, 115004 (2024)
13. W.S. Arsyad, et al., *J. Mol. Struct.* **1303**, 137548 (2024)
14. N.L. Tarwal, et al., *Chinese J. Phys.* **73**, 581 (2021)
15. M. Ayaz, M. Hijji, A.S. Alatawi, M.A. Namazi, M.I.M. Ershath, *J. Phys. Chem. Solids* **188**, 111913 (2024)
16. K.R. Aneesiya, C. Louis, *J. Alloys Compd.* **829**, 154497 (2020)
17. S. Dayan, N. Kayaci, N. Kalaycioğlu Özpozan, *J. Mol. Struct.* **1209**, 127920 (2020)
18. R. Bashir, A.R. Makhdoom, M.K. Bilal, M. Ahmad Badar, *Optik (Stuttg.)* **157**, 11 (2018)
19. K. Wongcharee, V. Meeyoo, S. Chavadej, *Sol. Energy Mater. Sol. Cells* **91**(7), 566 (2007)
20. F.C. Ferreira, R.S. Babu, A.L.F. de Barros, S. Raja, L.R.B. da Conceição, L.H.C. Mattoso, *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.* **233**, 118198 (2020)
21. S. Rivera-Calderón, et al., *Mater. Lett.* **315**, 131988 (2022)
22. U. Mahajan, K. Prajapat, M. Dhone, K. Sahu, P.M. Shirage, *Nano-Structures & Nano-Objects* **37**, 101111 (2024)
23. Ü. Özgür, et al., *J. Appl. Phys.* **98**(4) (2005)
24. J.H. Li, et al., *J. Lumin.* **122–123**, 352 (2007)
25. S. Sharifi Malvajerdi, et al., *ACS Appl. Mater. Interfaces* **13**(39), 46951 (2021)
26. Q. Zhao, et al., *J. Phys. Chem. C* **111**(45), 17136 (2007)
27. R. Larba, I. Boukerche, N. Alane, N. Habbache, S. Djerad, L. Tifouti, *Hydrometallurgy* **134–135**, 117 (2013)
28. I. Akbar, A.H. Yuwono, N. Sofyan, G. Ramahdita, A. Sholehah, *Int. J. Technol.* **6**(7), 1205 (2015)
29. P. Römkens, L. Bouwman, J. Japenga, C. Draaisma, *Environ. Pollut.* **116**(1), 109 (2002)
30. S.M. Hosseini, I.A. Sarsari, P. Kameli, H. Salamati, *J. Alloys Compd.* **640**, 408 (2015)
31. I.A. Mudunkotuwa, T. Rupasinghe, C.M. Wu, V.H. Grassian, *Langmuir* **28**(1), 396 (2012)
32. Z. Yang, Q.H. Liu, L. Yang, *Mater. Res. Bull.* **42**(2), 221 (2007)
33. T. Yoshida, M. Tochimoto, D. Schlettwein, D. Wöhrle, T. Sugiura, H. Minoura, *Chem. Mater.* **11**(10), 2657 (1999)
34. M.S. Yoo, B.R. James, *Soil Sci.* **168**(5), 356 (2003)

Open Access This chapter is licensed under the terms of the Creative Commons Attribution-NonCommercial 4.0 International License (<http://creativecommons.org/licenses/by-nc/4.0/>), which permits any noncommercial use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license and indicate if changes were made.

The images or other third party material in this chapter are included in the chapter's Creative Commons license, unless indicated otherwise in a credit line to the material. If material is not included in the chapter's Creative Commons license and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder.

