Indonesian Journal of Chemical Research

http://ojs3.unpatti.ac.id/index.php/ijcr Indo. J. Chem. Res., 10(2), 83-87, 2022

Determination of Band Gap Energy of ZnO/Au Nanoparticles Resulting in Laser Ablation in Liquid

Mardiana Julita[1], Muhandis Shiddiq[2*], Miftahul Khair[3*]

[1,3]Department of chemistry, Faculty of Mathematics and Natural Science, Universitas Negeri Padang, Jl. Prof. Hamka, Padang 25131, Indonesia.
[2]Physics Research Center, National Research and Innovation Agency, Building 442 Puspiptek, South Tangerang, Banten 15314

[*]*Corresponding Author: miftah@fmipa.unp.ac.id; muhandis.shiddiq@gmail.com*

Received: July 2022
Received in revised: July 2022
Accepted: August 2022
Available online: September 2022

Abstract

The synthesis of ZnO and ZnO/Au nanoparticles using the laser ablation method in liquid has been successfully carried out. Characterizing the optical properties of ZnO and ZnO/Au using a UV-Vis Spectrophotometer (Ocean Optic MAYA Pro 2000) measured in the wavelength range of 275-875 nm. The characterization results obtained are absorbance and band gap values of ZnO and ZnO/Au nanoparticles. This study found the absorbance values of ZnO nanoparticles at wavelengths 330 and 335 nm. After obtaining the absorbance value, the band gap value was analyzed for ZnO and ZnO/Au nanoparticles, respectively, 3.23 eV and 3.17 eV. The decrease in the band gap value in ZnO is due to the presence of Au in ZnO nanoparticles which can replace one of the lattices in the ZnO crystal structure.

Keywords: Band gap, nanoparticle, ZnO/Au, laser ablation, crystal.

INTRODUCTION

Zinc Oxide (ZnO) is a metal oxide that is a semiconductor with a wide band gap (3.37 eV) and has violet absorption in the ultraviolet (UV) at room temperature (Fageria et al., 2014). ZnO is considered one of the most widely used metal oxides for various applications today. In particular, ZnO can be used as optoelectronic, piezoelectric, and photochemical materials. ZnO is a multifunctional material because of its outstanding properties, high resistance efficiency, high absorbance peak in the UV region, piezoelectric crystals, transparency, and good electrical conductivity (Jaber et al., 2021). In addition, various ZnO nanostructures such as ZnO nanorods, nanowires, nanobelts, nanocombs, and nanoparticles (NPs) can be synthesized and studied for their optical properties. They can be adapted by changing their morphology, structure, size, and surface state. ZnO in the form of nanoparticles is one of the ZnO nanostructures that has attracted much attention because it has more potential in its application. In addition, doping and surface decoration can change the properties of ZnO nanoparticles, expanding the application scope of ZnO nanoparticles and improving the performance of ZnO-based applications. In the photovoltaic field, ZnO nanoparticles and composites containing ZnO nanoparticles are considered promising metal oxides (Chen et al., 2020).

ZnO nanoparticles have the potential for photocatalytic applications (Mulyati & Panjaitan, 2021). The ZnO nanoparticle photocatalytic performance can be improved by doping, decorating, or forming heterostructures with other materials (Yao et al., 2021). However, ZnO has a significant disadvantage as a photocatalyst, namely its low charge separation efficiency. Therefore, efforts have been made to modify the physical and chemical properties of ZnO by introducing metal impurities to shift the ZnO valence band gap to the conduction band region and reduce the band gap energy to the UV region (Kumar, 2017). Increasing the photocatalytic activity of ZnO as a catalyst can be doped with precious metals. Doping is a way to change the electrical and optical properties of semiconductors. Doping is done to increase the conductivity of ZnO. In this study, the starting metal to be used is Au. Au is an element that can be used as a dopant because it can be an absorber to collect electrons from the ZnO conduction band (Rutu et al., 2020), and it is essential in inhibiting electron recombination. The precious metal doped ZnO will affect the optical and structural properties (Pathak et al., 2018).

Many methods can synthesize nanoparticles (Taba et al., 2019). One of them is synthesizing ZnO nanoparticles using a laser ablation method in a liquid. The laser ablation method in liquid is a simple method to produce nanoparticles. Laser ablation has several advantages compared to other techniques. The nanoparticles produced are of high purity because they do not involve chemicals during the synthesis process and only require pure metal and a liquid medium such as deionized water (Avicenna et al., 2021). The laser ablation mechanism depends on the physical properties of the metal and the environmental medium. The ablation of metal begins with the absorption of laser light energy. When the laser beam interacts with a metal target, it will photoionize the metal. Afterward, the metal nanoparticles will be released from the metal plate in different phases depending on the absorbed energy (Reza Sadrolhosseini et al., 2019).

Based on the explanation above, ZnO/Au has been synthesized using the laser ablation method in liquid and will determine the change in band gap value between ZnO and ZnO nanoparticles doped with Au.

METHODOLOGY

Materials and Instrumentals

The tools used in this research are Nd: YAG laser, Analytical Balance, UV-Vis Spectrophotometer (Ocean Optic MAYA Pro 2000), micropipette, glass equipment: measuring flask, measuring pipette, measuring cup, Erlenmeyer and beaker. As for the materials used in this study, namely the Zn Plate (1.6 x 1.6 cm) with a plate thickness of ±3mm, the Au plate (99.9%) with a plate thickness of ±3mm, and the solution used in the synthesis process, namely aquabidest.

Methods

Synthesis of ZnO/Au. Nanoparticles

The synthesis of ZnO/Au nanoparticles using the laser ablation method in a liquid was carried out in two stages. This method is by research by (Anugrahwidya *et al*., 2020). First, the zinc plate was ablated for 30 minutes (pure ZnO and ZnO/Au samples). The resulting ZnO colloid will be used for Au plate ablation. Second, the Au plate was ablated in ZnO colloid for 1 minute to produce ZnO/Au nanoparticles (Figure 1). Furthermore, the band gap values between ZnO and ZnO/Au nanoparticles will be analyzed. The band gap values are derived from absorbance and wavelength data obtained from UV-Vis measurements.

Figure 1. (a) ZnO nanoparticle (b) ZnO/Au nanoparticle

Absorbance Measurement using UV-Vis

The absorbance values of ZnO and ZnO/Au nanoparticles were measured using a UV-Vis Spectrophotometer (Ocean Optic MAYA Pro 2000). Characterization using UV-Vis aims to obtain absorbance in the wavelength range of 275-825 nm. Thus, the band gap value of each sample can be determined using the Tauc Plot method.

RESULTS AND DISCUSSION

The Optical Properties Characterization of ZnO doping Au and ZnO Nanoparticles.

ZnO and ZnO/Au nanoparticles synthesized by laser ablation method in liquid were characterized using a UV-Vis spectrophotometer (Ocean Optic MAYA Pro 2000) at a wavelength of 275-825 nm. The measurement aims to determine the absorbance and band gap values of ZnO and ZnO/Au nanoparticles. The absorbance spectra of ZnO and ZnO/Au nanoparticles are presented in Figure 2.

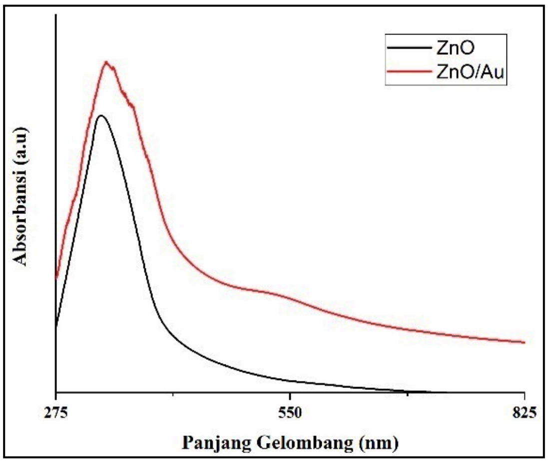


Figure 2. Graph of the absorbance spectra of ZnO and ZnO/Au nanoparticles

Based on the graph in Figure 2, it can be seen that the absorbance values of ZnO nanoparticles are at wavelengths 330 and 335 nm. The absorbance value of Au is at a wavelength of 525 nm. This number shows that the absorbance of ZnO nanoparticles is in the ultraviolet region and is in line with research that has been carried out by (Yudasari et al., 2021) showed that ZnO nanoparticles had absorbance values at wavelengths between 300 to 400 nm. This condition is caused by the absorption of the ZnO semiconductor when electrons move from the valence band (VB) to the conduction band (CB) (Anugrahwidya et al., 2020)

At each addition of the ablation time, the wavelength shifts to the right or towards the redshift area. The wavelength values obtained respectively 330 nm and 335 nm, as shown in Figure 2. This result is because, when Zn metal is ablated, Zn nanoparticles will be released from the metal surface subjected to the laser, causing a change in the crystal structure of Zn. The resulting nanoparticles will come out and spread in the liquid (aquabidest) and oxidize with the surrounding oxygen. When the Au atoms are doped to ZnO, the Au atoms will occupy the Zn position in the ZnO lattice (Sathya et al., 2017).

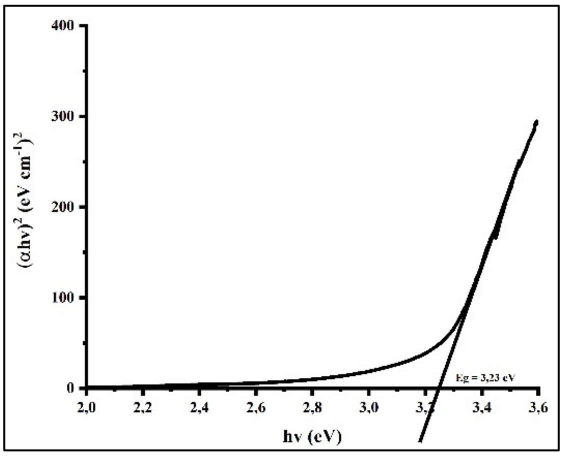
Determination of Band gap Value of ZnO and ZnO/Au Nanoparticles

Based on the data from UV-Vis measurements that have been obtained, these data are used to determine the band gap value of ZnO and ZnO/Au nanoparticles using the Tauc Plot method as in equations (1) and (2) (Makuła et al., 2018)

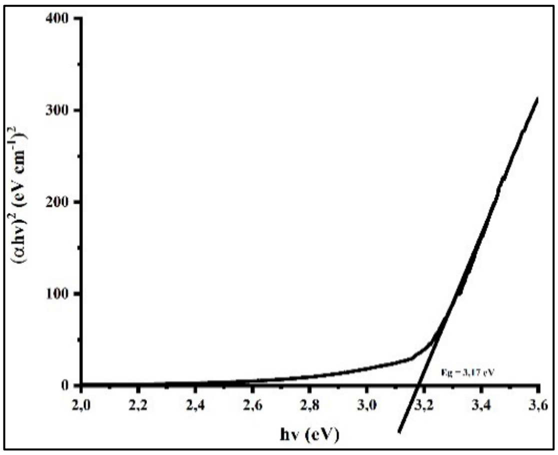
$$E_g = \frac{h\upsilon}{\lambda} \tag{1}$$

$$\alpha h\upsilon = (2{,}303 \times A \times h\upsilon)^n \tag{2}$$

With the speed of light, h Planck's constant, wavelength, α is the absorption coefficient, A is the proportional constant, E_g is the band gap energy value, and n indicates the nature of the electron transition. If the sample used is a direct band gap, then n=1//2 while the model, which is an indirect band gap, has a value of n=2 (Kumar, A, 2017). Because the sample used is an indirect band gap, then n=2. Then the relationship between hυ and $(\alpha h\upsilon)^2$ will be plotted (Daniyati et al., 2015). The band gap value is on the x-axis. The comparison of the band gap values between ZnO and ZnO/nanoparticles is presented in Figure 3.



(a)



(b)

Figure 3. Band gap plot (a) ZnO (b) ZnO/Au

Based on the graph in Figure 3, the band gap value for ZnO is 3.23 eV, and ZnO/Au is 3.17 eV. The decrease in the energy gap is in line with the increase in concentration (the length of ablation time given); the quality of the synthesized sample can cause this. The longer ablation time causes the resulting colloid to be more purplish because of the Au atoms involved. The energy gap shows electrons moving from the valence band to the conduction band. The smaller the band gap value indicates that more electrons move in the excitation area so that it can affect the absorbance intensity of the nanoparticles. The absorbance intensity shows the transition activity from the excitation region to the ground state. Changes in the band gap value occur due to the presence of Au in the ZnO nanoparticle structure. The Au atom can replace one of the lattices in the ZnO crystal structure, namely hexagonal wurtzite, so that it can change the crystallinity of

ZnO, characterized by a reduced band gap energy value (Ayuwulanda et al., 2021).

CONCLUSION

In this study, it can be concluded that the absorbance value of ZnO nanoparticles is in the wavelength range of 330-335 nm, and the absorbance value of Au is in the wavelength of 525 nm. The band gap value of ZnO decreased after being doped with Au from 3.23 eV to 3.17 eV. The decrease in the band gap value in ZnO occurs because the presence of Au in ZnO can be substituted in one of the ZnO crystal structure lattices.

ACKNOWLEDGMENT

Acknowledgments are given to the National Research and Innovation Agency for the funding granted for this research. Thanks to Mr. Dr. Muhandis Shiddiq from the BRIN Physics Research Center for his assistance in guiding the author during the research. The author would also like to thank Mr. Miftahul Khair, M.Sc., Ph.D., who also conducted the author in completing this research.

REFERENCES

Anugrahwidya, R., Yudasari, N., & Tahir, D. (2020). Optical and Structural Investigation of Synthesis ZnO/Ag Nanoparticles Prepared By Laser Ablation in Liquid. *Materials Science in Semiconductor Processing*, *105*. https://doi.org/ 10.1016/j.mssp.2019.104712

Avicenna, S., Nurhasanah, I., & Khumaeni, A. (2021). Synthesis of Colloidal Silver Nanoparticles in Various Liquid Media Using Pulse Laser Ablation Method and Its Antibacterial Properties. *Indones. J. Chem.*, *21*(3), 761–768. https://doi.org/ 10.22146/ ijc.60344

Ayuwulanda, A., Saputro, A. H., Permana, Y. N., & Saputra, S. (2021). Green Dekorasi Au/ZnO Nanokomposit Melalui Media Ekstrak Daun Gaharu (Aquilaria Malaccenensis L.) dan Penentuan Nilai Sun Protection Factor. *Jurnal Kimia Dan Kemasan*, *43*(2), 126–132.

Chen, W., Yao, C., Gan, J., Jiang, K., Hu, Z., Lin, J., Xu, N., Sun, J., & Wu, J. (2020). ZnO Colloids and Zno Nanoparticles Synthesized by Pulsed Laser Ablation of Zinc Powders in Water. *Materials Science in Semiconductor Processing*, *109* (December 2019), 104918. https://doi.org/10.1016/j.mssp.2020.104918

Daniyati, R., Zharvan, V., & Pramono, Y. H. (2015). Penentuan Energi Celah Pita Optik Film TiO_2 Menggunakan Metode Tauc Plot. *Seminar Sains Dan Teknologi*, *August*, 1–5.

Fageria, P., Gangopadhyay, S., & Pande, S. (2014). Synthesis of ZnO/Au and ZnO/Ag Nanoparticles and Their Photocatalytic Application Using UV and Visible Light. *RSC Advances*, *4*(48), 24962–24972. https://doi.org/ 10.1039/c4ra03158j

Jaber, G. S., Khashan, K. S., & Abbas, M. J. (2021). Study The Antibacterial Activity of Zinc Oxide Nanoparticles Synthesis by Laser Ablation in Liquid. *Materials Today: Proceedings*, *42*, 2668–2673. https://doi.org/10.1016/j.matpr. 2020.12.646

Kumar, A. (2017). A Review on The Factors Affecting The Photocatalytic Degradation of Hazardous Materials. *Material Science & Engineer. Inter. J.*, *1*(3). https://doi.org/ 10.15406/mseij.2017.01.00018

Makuła, P., Pacia, M., & Macyk, W. (2018). How To Correctly Determine the Band Gap Energy of Modified Semiconductor Photocatalysts Based on UV-Vis Spectra. *Journal of Physical Chemistry Letters*, *9*(23), 6814–6817. https://doi.org/10.1021/acs.jpclett.8b02892

Mulyati, B., & Panjaitan, R. S. (2021). Karakterisasi Fotokatalis Untuk Fotoreduksi Karbon Dioksida Menjadi Asam Format Dalam Fasa Akuatik. *Indo. J. Chem. Res*, *9*(2), 129–136. https://doi.org/10.30598//ijcr.2020.8-jen

Pathak, T. K., Kroon, R. E., & Swart, H. C. (2018). Photocatalytic and Biological Applications of Ag and Au Doped Zno Nanomaterial Synthesized by Combustion. *Vacuum*, *157*, 508–513. https://doi.org/10.1016/j.vacuum. 2018. 09.020

Rutu, I., Zakir, M., & Budi, P. (2020). Sintesis Nanopartikel Perak dan Pengaruh Penambahan Asam p-Kumarat Untuk Aplikasi Deteksi Melamin. *Indo. J. Chem. Res.*, *7*(2), 141–150. https://doi.org/10.30598//ijcr.2020.7-irw

Reza Sadrolhosseini, A., Adzir Mahdi, M., Alizadeh, F., & Abdul Rashid, S. (2019). Laser Ablation Technique for Synthesis of Metal Nanoparticle in Liquid. *Laser Technology and Its Applications*. Chapter 4. https://doi.org/ 10.5772/intechopen.80374

Sathya, B., Benny Anburaj, D., Porkalai, V., & Nedunchezhian, G. (2017). Raman Scattering And Photoluminescence Properties of Ag Doped ZnO Synthesized by Sol-Gel Method. *J. Materials Science: Materials in Electronics*, *28*(8), 6022–6032. https://doi.org/10.1007/s10854-016-6278-3

Taba, P., Parmitha, N. Y., & Kasim, S. (2019). Synthesis of Silver Nanoparticles Using *Syzygium polyanthum* Extract as Bioreductor and the Application as Antioxidant. *Indo. J. Chem. Res.*, *7*(1), 51–60.

Yao, C., Chen, W., Li, L., Jiang, K., Hu, Z., Lin, J., Xu, N., Sun, J., & Wu, J. (2021). ZnO: Au Nanocomposites With High Photocatalytic Activity Prepared by Liquid-Phase Pulsed Laser Ablation. *Optics and Laser Technology*, *133*, 106533. https://doi.org/10.1016/j.optlastec.2020.106533

Yudasari, N., Anugrahwidya, R., Tahir, D., Suliyanti, M. M., Herbani, Y., Imawan, C., Khalil, M., & Djuhana, D. (2021). Enhanced Photocatalytic Degradation of Rhodamine 6G (R6G) Using ZnO–Ag nanoparticles Synthesized By Pulsed Laser Ablation in Liquid (PLAL). *J. Alloys and Compounds*, *886*, 161291. https://doi.org/10.1016/j.jallcom.2021.161291