EFFECT OF ADDITIONAL Ni METAL DOPANTS ON OPTICAL ABSORPTION PROPERTIES AND CRYSTAL STRUCTURE OF ZnO PHOTOCATALYST MATERIALS

Istiroyah*, H. Harsono, M. Nurhuda, T.S. Utami, A.A. Dardiri, Y. Engge, F. Maulana

Department of Physics, Mathematics and Natural Science of Faculty,
Brawijaya University Malang
Jl. Veteran Malang 65145, Indonesia

Received: 13rd September 2022 ; Revised:24th February 2023 ; Accepted: 28th March 2023

ABSTRACT

The addition of Ni metal dopants to the ZnO photocatalyst material has been carried out using the immersion method followed by sonication. The variables observed included variations in the concentration of addition of Ni and sonication time. The results of the optical absorption analysis from the uv-vis test showed that the optimum condition was reached at a concentration of 25% Ni and a sonication time of 30 minutes. The optical absorption peak has shifted towards the wavelength of visible light and new absorption peaks have been observed in the wavelength range of 425-450 nm and 650-750 nm. The energy band gap also decreased from 3.22 eV to 3.09 eV. While the crystal size analysis of the XRD diffraction pattern showed a decrease in the crystal size at 25%Ni from 105.012nm to 78.545nm.

Keywords: ZnO; photocatalyst; band gap; crystal structure; absorption peak and water splitting

Introduction

Research on hydrogen dissociation from water is a new energy alternative, renewable and environmentally friendly. This research and exploration are now one of the most intensive studies worldwide. World energy demand which is predicted to reach 739 million quadrillion BTUs in 2035[1] is a challenge for energy sustainability. Even in Indonesia, with a population of 271,349,889 people[2] and the development of the technology it uses also has challenges in meeting its energy needs. Based on data from Indonesia's 2014 Energy Outlook Book (OEI 2014) in 2033, total domestic energy production (fossil and EBT) will no longer be able to meet domestic consumption due to limited energy resources so Indonesia will become a net energy importer country for the basic scenario. The solution to overcome this problem is the development of sustainable technology in terms of finding alternative energy sources that are more environmentally friendly and renewable energy.

*Corresponding author.
E-Mail: istie@ub.ac.id

The electrolysis process to dissociate hydrogen from water requires a very large consumption of electrical energy so it is not economically feasible. On the other hand, photocatalytic processes that use sunlight to dissociate hydrogen from water also provide low yields. The combination of processes has been expected to give better results. The photocatalytic process will increase the effectiveness of the hydrogen dissociation process so that electrical energy consumption decreases during the process.

Photocatalysis using semiconductors was first introduced by Fujishima and Honda in 1972.[3] The semiconductor material used is TiO_2. However, TiO_2 has several drawbacks that limit its use, such as a wide band gap and a high rate of charge carrier recombination.[4] So the researchers developed various other alternative photocatalyst materials such as ZnO.

ZnO is a metal oxide such as TiO_2 and has several advantages, namely its abundant availability in nature, non-toxic, high thermal

and chemical stability, low cost, high catalytic activity, and high quantum yield.[5-6] The characteristic that makes ZnO superior to TiO_2 is that ZnO has a high level of electron mobility, which is 200-300 cm2V-1s-1 or 10-100 times higher than TiO_2, lower recombination rate and is easier to synthesize to obtain different morphologies.[7] In addition, the ZnO semiconductor can absorb solar UV rays better than other semiconductors such as TiO_2. TiO_2 is only able to absorb UV ± 4%, while ZnO ± 10% for the photocatalytic process. This is related to the surface morphology of ZnO which leads to better energy conversion.

ZnO has a wide energy band gap of about 3.37 eV[8] so it is only effective in the UV spectrum and low particle surface area. Various methods for modification have been developed, such as sol-gel,[5-6] thermal decomposition,[9-12] co-precipitation,[13] sonochemical,[14-16] and immersion-sonification. The immersion-sonication method is a simple and low-cost method. This method has succeeded in reducing the energy band gap of TiO_2 from 3.2 to 2.79 eV.[17] This simple and low-cost method will be developed in this study to modify ZnO in engineering its energy band gap and crystal size. Then studied, the effect of the addition of Ni on the optical absorption characteristics and crystal structure of the ZnO photocatalyst material.

This modification is expected to increase the photocatalytic activity of ZnO photocatalyst materials doped with nickel. The first increase in photocatalytic activity is indicated by a shift in optical absorption towards visible light wavelengths because most of the sunlight is visible light. Second, decreasing the band gap energy accelerates the transfer of electrons from the valence band to the conduction band, thereby demonstrating photocatalytic efficiency. Third, increasing the surface area of the particle becomes nano-sized, which will increase the number of valence electrons.

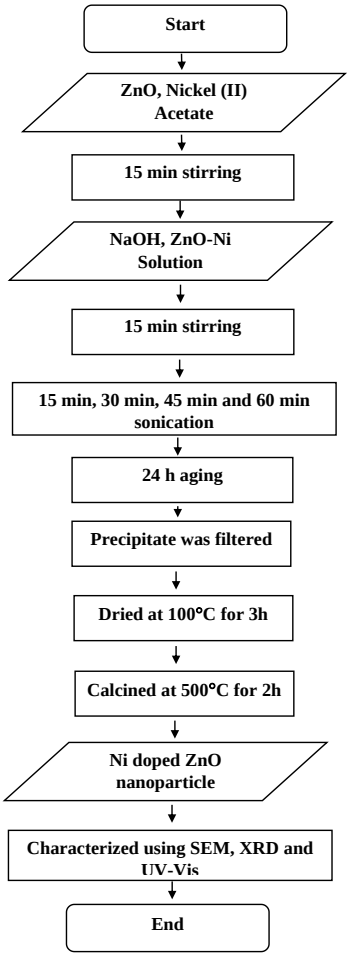


Figure 1. Flowchart of the synthesis of Ni-ZnO

Methods

The research was carried out by immersion-sonication method to modify the bandgap and microstructure of the ZnO photocatalyst material. Variations in sonication time and Ni concentration were observed variables. The stages of this research included material preparation, solution homogenization, sonication, soaking and precipitation, filtrate separation, drying, calcination, and characterization. The materials used included: ZnO pa powder, Nickel (II) nitrate hexahydrate, and NaOH.

The synthesis of Ni-ZnO was carried out by mixing ZnO powder and Nickel (II) Nitrate Hexahydrate. The mixture was dissolved in distilled water, and 1M NaOH was added. Then the solution was homogenized using a magnetic stirrer for 30 minutes. Then the solution was sonicated according to time

 ISSN:1979-6374/ EISSN:2460-5999

variations at room temperature. After that, the samples were aged for 24 hours. Then the sample was filtered and rinsed with distilled water to remove the sodium ion content. The precipitate was dried at a temperature of 60^{o}C for 1 hour and then calcined at a temperature of 400^{o}C for 2 hours. Furthermore, the analysis of optical characteristics using UV-vis spectroscopy. Meanwhile, analysis of crystal structure and crystal size was carried out by x-ray diffraction, and surface morphology by SEM-EDX.

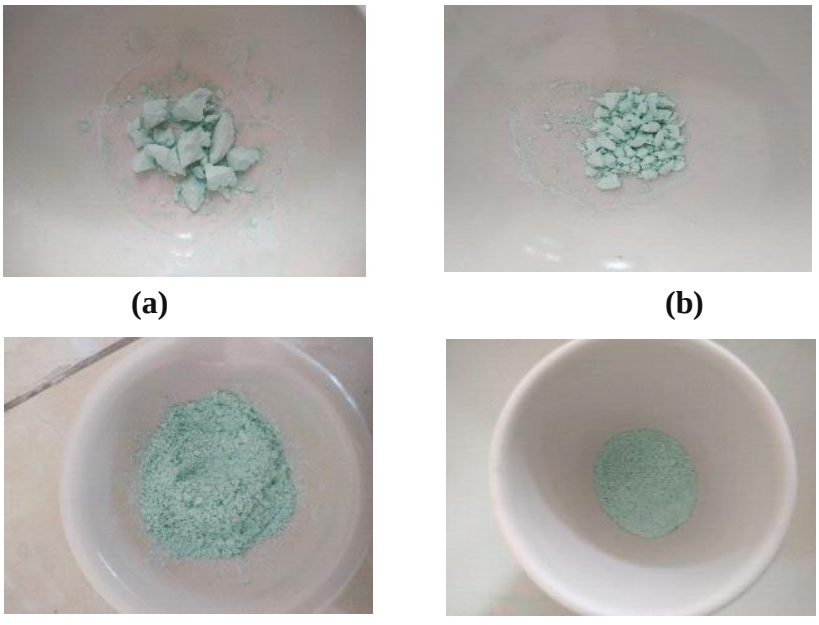
Result and Discussion

The process of adding Ni to ZnO was carried out by immersion method followed by a sonication process by exposure to ultrasonic waves. Through this process, it is expected that Ni will be able to infiltrate into ZnO so that Ni-ZnO material will be obtained. After the filtering process, a greenish-white powder was obtained as shown in Figures 2 a, b, and c.

After calcination, the colour of the sample changes to green, as shown in Figure 3.

(a) **(b)** **(c)**

Figure 2. Sample (a) 15 minutes sonication (b) 45 minutes sonication (c) 60 minutes sonication.



(a) **(b)**

(c) **(d)**

Figure 3. Sample (a) 15 minutes sonication (b) 60 minutes sonication after calcination (c) 45 minutes sonication (d) 60 minutes sonication after chrused

 ISSN:1979-6374/ EISSN:2460-5999

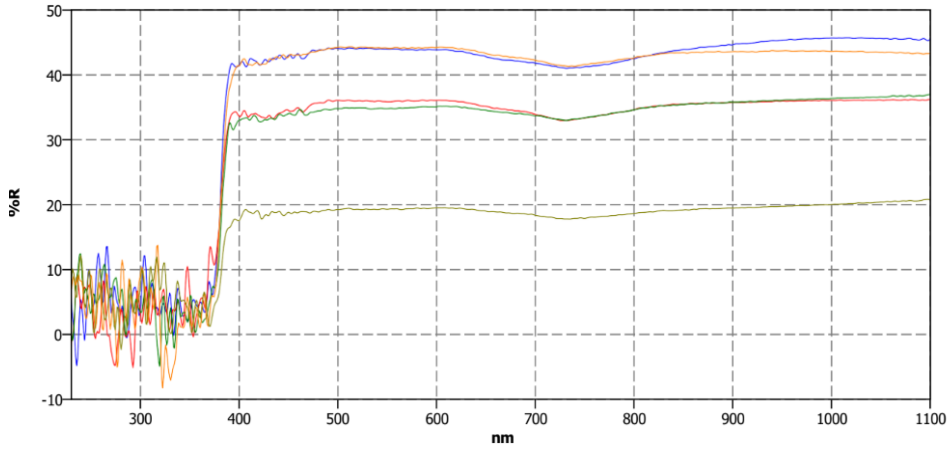


Figure 4. Ni-ZnO photocatalyst sample optical reflectance graph

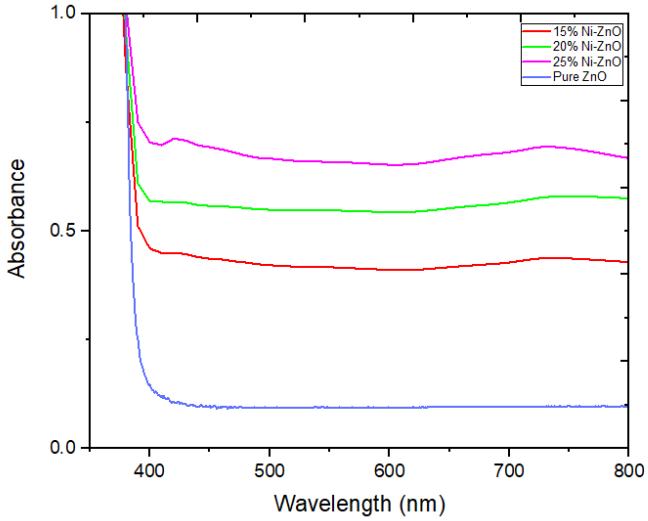


Figure 5. Optical absorption graph of the ZnO photocatalyst sample with variations in the addition of Ni 0, 15, 20, and 25%

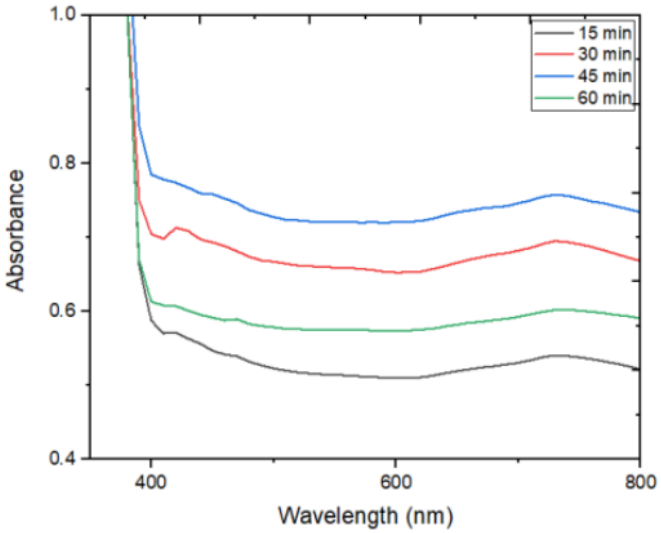


Figure 6. Optical absorption graph of ZnO photocatalyst samples with variations in sonication time of 15, 30, 45 and 60 minutes

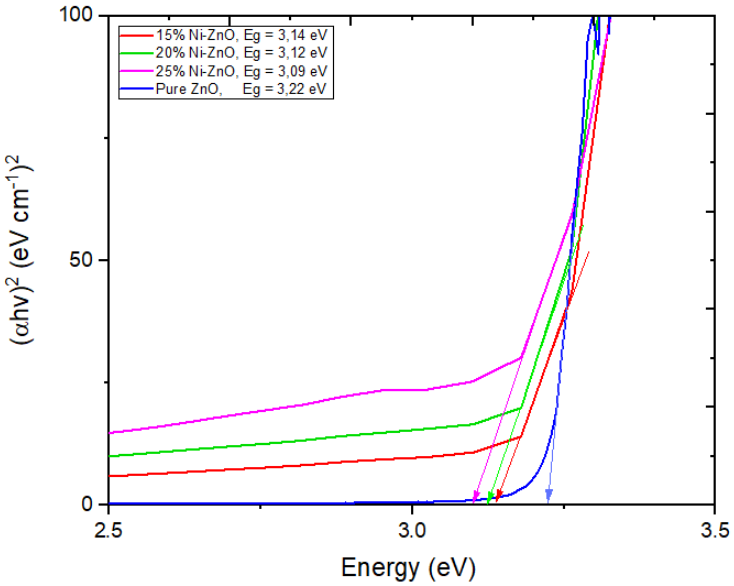


Figure 7. Graph of the width of the band gap of the ZnO photocatalyst sample with variations in the addition of Ni 0, 15, 20, and 25%

Optical absorption characteristics and energy band gap of Ni-ZnO

The UV-vis spectroscopy test was carried out to determine the optical absorption characteristics and the energy band gap width of the Ni-ZnO material.

The effectiveness of the optical activity of the photocatalyst material can be seen from the optical absorption and the energy band gap width. The analysis of the optical absorption graph gives results as can be seen in Figure 5.

The optical absorption graph of the ZnO photocatalyst material shows that the added dopant (Ni) has shifted the optical absorption peak towards the visible light wavelength.

The analysis of the optical absorption of Ni-ZnO material from Figures 5 and 6 gave optimal results at a concentration of 25% Ni addition, and a sonication time of 30 minutes. In these two parameters, the graph provides the characteristics of the optical absorption shift towards visible wavelengths (> 400 nm) and the phenomenon of the emergence of new peaks in the visible light range, namely in the range of wavelengths 425 -450 nm and 650 - 750 nm). Ni metal added to ZnO material will act as an electron donor to form a new band in the forbidden band region. This causes the Ni-ZnO material to be able to absorb photons in the visible light region.

This is expected to make the Ni-ZnO photocatalyst material more effective in the photocatalytic process using sunlight. This is also supported by the results of the analysis of the energy band gap of the Ni-ZnO photocatalyst material as shown in Figure 7. There is a decrease in the bandgap in ZnO along with an increase in the concentration of dopants used.

In the variation of sonication time shown in Figure 8, a decrease in the band gap occurred in 25% of Ni-ZnO which was sonicated within 15 to 60 minutes. When sonicated for 60 minutes, there was a widening of the band gap caused by a decrease in the intensity of Ni dopants added to the ZnO lattice. As a result, the electron density increases, and the band gap width increases.[18] This is because, at the time variation of 60 minutes, there is a band gap anomaly. Based on research by Rohman[23] states that an increase in sonication time can change the phase transition temperature of the ZnO semiconductor due to decreased electron lifetime, causing defects in the crystal. The presence of defects in the crystal can increase the emergence of electron-hole recombination. In addition, this is related to the emergence of a secondary phase in the form of the NiO phase. The presence of the secondary phase which is an impurity phase indicates that there is doping saturation in the

 ISSN:1979-6374/ EISSN:2460-5999

sample which results in heterogeneity in the sample thereby inhibiting the decrease in the value of the band gap.

Crystal structure and crystal size analysis

The crystalline phases of the pure ZnO and 25% Ni-ZnO samples were analyzed by XRD, and the corresponding diffraction patterns are shown in Figure 9.

All the diffraction peaks of the pure ZnO and 25% Ni-ZnO samples were indexed according to data from the database sheet JCPDS (ref. 01- 079-2205) showed that pure ZnO and 25% Ni-ZnO had a hexagonal wurtzite crystal structure. The diffraction peaks of the pure ZnO structure at 2θ from 31.8°, 34.4°, 36.4°, 47.6°, 62.9°, 66.6°, 67.9° and 69.2° set to (100), (002), (101), (102), (103), (112) and (201). With the intensity of the 2θ highest sample pure ZnO on the lattice plane (101) with an angle of 36.4º.

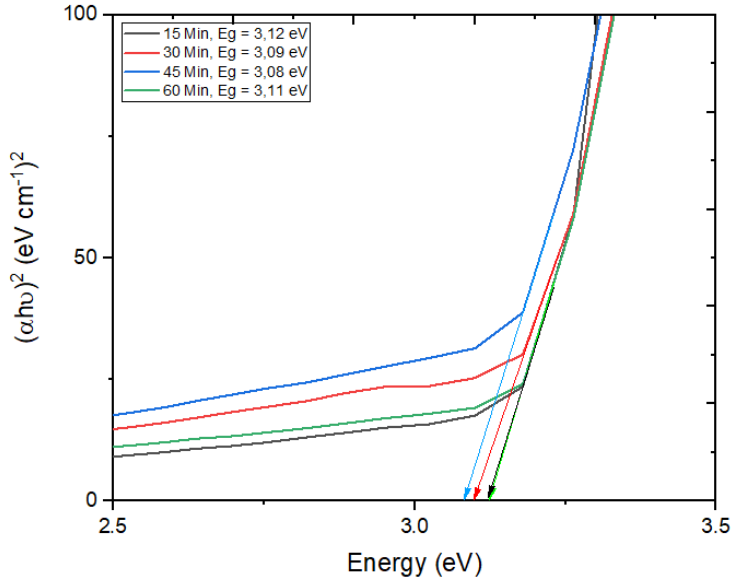


Figure 8. Graph of the band gap width of the ZnO photocatalyst sample with variations in sonication time of 15, 30, 45, and 60 minutes

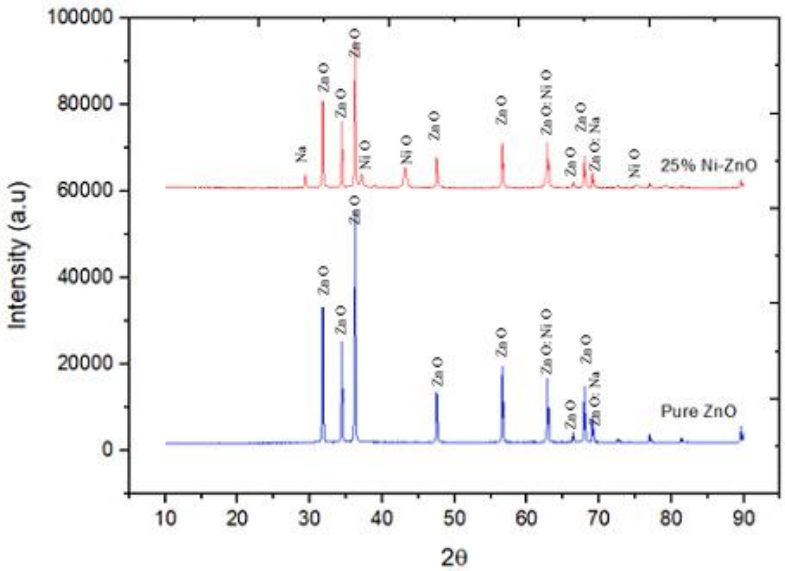


Figure 9. XRD pattern of pure ZnO and ZnO photocatalyst samples with 25% Ni addition concentration.

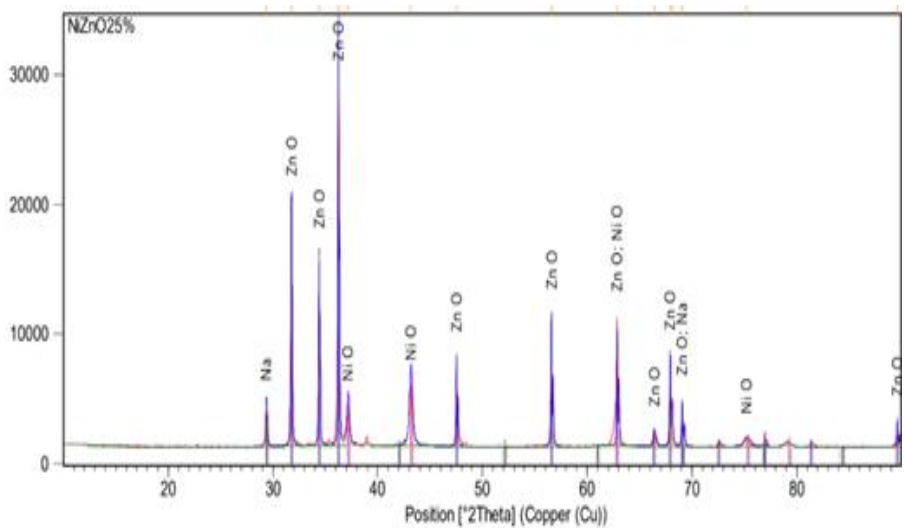


Figure 10. X-Ray Diffraction Peak Analysis of 25% Ni - ZnO sample

Table 1. Lattice parameter size and crystal size in pure ZnO and 25% Ni-ZnO

Ni Concentration	Lattice parameters (Å)		D (nm)
	a=b	c	
0%	3,250	5,207	105,01
25%	3,251	5,212	78,545

Based on the XRD pattern images of the 25% Ni-ZnO, it can be seen that the diffractogram peaks show the lattice plane with a diffraction angle of 31.76º; 34.42º; 36.25º; 47.55º; 56.62º; 62.89º; 67.99º; 69.11º with the highest intensity 2 of the ZnO sample in the lattice plane with an angle of 36.25º. After the addition of 25% Ni, there is a new diffraction peak at angles 2θ=37,15º and 43,15º which matches the peak of NiO based on the reference from the database sheet (ref. 01-073-1523). The presence of NiO diffraction peaks is due to the solubility of the Ni dopant exceeding the solubility threshold of ZnO as the host matrix.[19]

The addition of 25% Ni caused a decrease in the intensity of each ZnO diffraction peak. This indicates a distortion in the lattice caused by the presence of amorphous NiO and/or the presence of segregation of Ni atoms at grain boundaries.[20] The presence of NiO also affects the size of the lattice parameters.

Table 1 shows an increase in the size of the lattice parameters after the addition of Ni. The increase in the size of this lattice parameter can be caused by the size of Ni^{2+} (0.83 nm) originating from NiO which is larger than the size of Zn^{2+} (0.74 nm) as the host lattice.[21]

The average crystal size of pure ZnO and 25% Ni-ZnO was measured using the Deybe Scherrer equation which is tabulated in Table 1. These measurements show the results where the average crystal size decreases due to the addition of Ni dopant. A report from the study of Raj *et al*,[22] stated that the addition of nickel dopant was able to inhibit the growth of ZnO and reduce the crystal size of ZnO. As a result of the smaller crystal size, the surface area will increase, resulting in an increase in the photocatalytic activity of ZnO.

This can be caused by the use of sonication methods during the synthesis process and the use of nickel as a dopant.[23] In addition, this is related to the prevention of particle growth which includes inhibition of grain boundary motion. In the process of synthesizing Ni-ZnO nanoparticles during preheating (low temperature) crystal growth has not occurred because the movement of the grain boundaries is restrained by the undissolved elementary material particles. Grain boundaries are meeting points for the growth of particles of

 ISSN:1979-6374/ EISSN:2460-5999

various nuclei. At higher temperatures, a grain formation process occurs which begins with the formation of groups of atoms on the surface of the liquid which then becomes the core of solid particles or commonly known as the nucleation process. During the chemical process, the core will be the first to increase in size due to the movement of the grain boundaries. The movement of grain boundaries can be prevented by the deposition of a secondary phase or by contaminating the ZnO surface. When grain boundary movement occurs accompanied by ion insertion events Zn^{2+} and ion substitution Ni^{2+}, the movement of grain boundaries will be hindered by the generation of deceleration forces. If the deceleration force is greater than the driving force for grain growth, the particles will not be able to grow anymore, so smaller size particles are obtained when adding dopants. So, the presence of Ni^{2+} in the ZnO lattice can be useful for preventing the growth of crystal grains. This is what causes the variation in crystal size with the addition of nickel dopant concentration in the Ni-ZnO nanoparticle samples.

Conclusion

Ni-ZnO was synthesized using the sonication method under various conditions. UV-vis analysis showed a narrowing of the band gap under certain conditions. The ZnO sample which was added with nickel with a concentration of 25% with a sonication time of 45 minutes, a sonication temperature of 30^o, and an immersion time of 24 hours had the smallest band gap. XRD results confirmed that pure ZnO and Ni added ZnO had a wurtzite crystal structure. SEM shows that the pure ZnO particles are spherical and oval in shape, while 25% Ni-ZnO has a more homogeneous shape, namely spherical. The EDX results showed the presence of other impurities in 25% Ni-ZnO, namely Na, C, and Al.

Acknowledgment

Thanks to the Central Laboratory of Biological Sciences (LSIH) Universitas Brawijaya and the Central Laboratory of the State University of Malang who have helped in the XRD and UV-Vis testing process. This research is financed through a Non-Lector Doctoral Research Grant for the Head of the Faculty of Science, Universitas Brawijaya for the 2021 Fiscal Year with contract no: 1613/UN10.F09/PN/2021

References

1. L.E. Doman, K.A. Smith, L.D. Mayne, E.M. Yucel, J.L. Barden, A.M. Fawzi, P.D. Martin, V.V. Zaretskaya, M.L. Mellish, D.R. Kearney, B.T. Murphy, K.R. Vincent, P.M. Lindstrom, M.T. Leff, 2010, International Energy Outlook 2010.
2. Badan Pusat Statistik. 2021. Sensus Penduduk 2020.
3. Daulbayev C, Sultanov F, Bakbolat B, Daulbayev O. 0D, 1D and 2D nanomaterials for visible photoelectrochemical water splitting. A Review. International Journal of Hydrogen Energy. 2020 Nov 27;45(58):33325-42.
4. Pavithra M, Raj MJ. Influence of ultrasonication time on solar light irradiated photocatalytic dye degradability and antibacterial activity of Pb doped ZnO nanocomposites. Ceramics International. 2021 Nov 15;47(22):32324-31. https://doi.org/10.1016/j.ceramint.2021.08.128
5. Ahmad I, Ahmed E, Ahmad M, Akhtar MS, Basharat MA, Khan WQ, Ghauri MI, Ali A, Manzoor MF. The investigation of hydrogen evolution using Ca doped ZnO catalysts under visible light illumination. Materials Science in Semiconductor Processing. 2020 Jan 1;105:104748.
6. Manzoor MF, Ahmed E, Ahmad M, Ahmad I, Rana AM, Ali A, Ghouri MI, Manzoor MS, Aziz MT. Enhanced photocatalytic activity of hydrogen evolution through Cu-incorporated ZnO nanocomposites. Materials Science in Semiconductor Processing. 2020 Dec 1;120:105278.
7. Ghorbani M, Abdizadeh H, Taheri M, Golobostanfard MR. Enhanced photoelectrochemical water splitting in

hierarchical porous ZnO/Reduced graphene oxide nanocomposite synthesized by sol-gel method. International Journal of Hydrogen Energy. 2018 Apr 19;43(16):7754-63.
8. Desai MA, Vyas AN, Saratale GD, Sartale SD. Zinc oxide superstructures: recent synthesis approaches and application for hydrogen production via photoelectrochemical water splitting. international journal of hydrogen energy. 2019 Jan 22;44(4):2091-127.
9. Lin CC, Li YY. Synthesis of ZnO nanowires by thermal decomposition of zinc acetate dihydrate. Materials Chemistry and Physics. 2009 Jan 15;113(1):334-7.
10. Wu M, Chen WJ, Shen YH, Huang FZ, Li CH, Li SK. In situ growth of matchlike ZnO/Au plasmonic heterostructure for enhanced photoelectrochemical water splitting. ACS applied materials & interfaces. 2014 Sep 10;6(17):15052-60.
11. Gnanamozhi P, Renganathan V, Chen SM, Pandiyan V, Arockiaraj MA, Alharbi NS, Kadaikunnan S, Khaled JM, Alanzi KF. Influence of Nickel concentration on the photocatalytic dye degradation (methylene blue and reactive red 120) and antibacterial activity of ZnO nanoparticles. Ceramics International. 2020 Aug 1;46(11):18322-30.
12. Donkova B, Vasileva P, Nihtianova D, Velichkova N, Stefanov P, Mehandjiev D. Synthesis, characterization, and catalytic application of Au/ZnO nanocomposites prepared by coprecipitation. Journal of materials science. 2011 Nov;46:7134-43.
13. Ahmad I, Ahmed E, Ahmad M, Akhtar MS, Basharat MA, Khan WQ, Ghauri MI, Ali A, Manzoor MF. The investigation of hydrogen evolution using Ca doped ZnO catalysts under visible light illumination. Materials Science in Semiconductor Processing. 2020 Jan 1;105:104748.
14. Bordbar M, Forghani-Pilerood S, Yeganeh-Faal A, Khodadadi B. Effect of morphology on the photocatalytic behavior of ZnO nanostructures: low temperature sonochemical synthesis of Ni doped ZnO nanoparticles. Journal of Nanostructures. 2016 Jul 1;6(3):190-8.
15. Singh B, Kaushal A, Bdikin I, Saravanan KV, Ferreira JM. Effect of Ni doping on structural and optical properties of Zn1− xNixO nanopowder synthesized via low cost sono-chemical method. Materials Research Bulletin. 2015 Oct 1;70:430-5.
16. Kandjani AE, Tabriz MF, Pourabbas BJ. Sonochemical synthesis of ZnO nanoparticles: The effect of temperature and sonication power. Materials Research Bulletin. 2008 Mar 4;43(3):645-54.
17. Singh B, Kaushal A, Bdikin I, Saravanan KV, Ferreira JM. Effect of Ni doping on structural and optical properties of Zn1− xNixO nanopowder synthesized via low cost sono-chemical method. Materials Research Bulletin. 2015 Oct 1;70:430-5. Available from: http://dx.doi.org/10.1016/j.materresbull.2015.05.009
18. Agus SA, Sudaryanto S. Penambahan N Pada TiO2 dan Pengaruhnya Pada Energi Band Gap TiO2 Sebagai Bahan Pengolah Limbah. InProsiding Seminar Nasional Teknologi dan Aplikasi Reaktor Nuklir 2016 (pp. 59-64).
19. Bouaoud A, Rmili A, Ouachtari F, Louardi A, Chtouki T, Elidrissi B, Erguig H. Transparent conducting properties of Ni doped zinc oxide thin films prepared by a facile spray pyrolysis technique using perfume atomizer. Materials Chemistry and Physics. 2013 Jan 15;137(3):843-7. Available from: http://dx.doi.org/10.1016/j.matchemphys.2012.10.023
20. Raj IL, Christy AJ, Prabu RD, Chidhambaram N, Shkir M, AlFaify S, Khan A. Significance of Ni doping on structure-morphology-photoluminescence, optical and photocatalytic activity of CBD grown ZnO nanowires for opto-photocatalyst applications. Inorganic Chemistry Communications. 2020 Sep 1;119:108082. https://doi.org/10.1016/j.inoche.2020.108082
21. Gnanamozhi P, Renganathan V, Chen SM, Pandiyan V, Arockiaraj MA, Alharbi NS, Kadaikunnan S, Khaled JM, Alanzi KF.

 ISSN:1979-6374/ EISSN:2460-5999

Influence of Nickel concentration on the photocatalytic dye degradation (methylene blue and reactive red 120) and antibacterial activity of ZnO nanoparticles. Ceramics International. 2020 Aug 1;46(11):18322-30. https://doi.org/10.1016/j.ceramint.2020.05.054

22. Samanta A, Goswami MN, Mahapatra PK. Magnetic and electric properties of Ni-doped ZnO nanoparticles exhibit diluted magnetic semiconductor in nature. Journal of alloys and compounds. 2018 Jan 5;730:399-407. Available from: https://doi.org/10.1016/j.jallcom.201.09.334
23. Rajbongshi BM, Ramchiary A, Samdarshi SK. Influence of N-doping on photocatalytic activity of ZnO nanoparticles under visible light irradiation. Materials Letters. 2014 Nov 1;134:111-4.
24. Sharifalhoseini Z, Entezari MH, Jalal R. Direct and indirect sonication affect differently the microstructure and the morphology of ZnO nanoparticles: Optical behavior and its antibacterial activity. Ultrasonics sonochemistry. 2015 Nov 1;27:466-73.