DOI: 10.51975/LNDP7232
Journal of the Nigerian Society of Chemical Engineers, 36(1), 2021

SYNTHESIS AND CHARACTERIZATION OF NEEM-BASED ZINC OXIDE PHOTOCATALYST

***Gana, I. N.[1,2], Ohageria, V.U.[1], Akpan, U.G.[1], Ani, I.J.[1]**
[1]Department of Chemical Engineering, Federal University of Technology, Minna, Nigeria
[2]Headquarters Central Armament Depot, Tactical Air Command, Nigerian Air Force Base, Makurdi, Nigeria
[*]Corresponding Author: ugaekon@futminna.edu.ng; ganaisraelndamawo@gmail.com

ABSTRACT

The use of chemicals for the synthesis of photocatalyts poses threat to the environment. In this study, an active photocatalyst, Dalbejiya Dongoyaro (Azadirachta indica)-based zinc oxide (ZnO) was biosynthesized from zinc acetate dihydrate using sol gel and precipitation methods. The synthesized samples were characterized using Fourier Transfer InfraRed (FTIR), X-Ray Diffractometry (XRD), Brunauer Emmet Teller (BET), Energy Dispersive X-ray Spectroscopy (EDS) and Scanning Electron Microscopy (SEM) characterization techniques. The XRD and SEM analysis of the green synthesized and non-green synthesized ZnO demonstrated the formation of hexagonal wurtzite crystalline structure and agglomerated morphology. EDX analysis demonstrated the existence of Zn and O as the major constituents of the as-synthesized nanoparticles with traces of carbon which could be attributed to the carbon tape of the sample holder. The BET analysis displayed that the surface area of the ZnO nanoparticles increased from 23.75 to 97.08 cm^3/g after the green synthesis. Based on the surface area values, it can be derived that neem leaf extract enhanced the surface area of the green synthesized sample. Green synthesis is a promising route for the synthesis of photocatalyst nanoparticle which is environmentally friendly and sustainable method.

Keywords: *Zinc oxide, Neem leaf extract, Photocatalyt, Degradation, Bio-synthesis*

1.0 INTRODUCTION

Photocatalysis is a photoinduced reaction which is accelerated in the presence of a catalyst (Akpan & Hameed, 2009), and the catalyst should be small enough (probably in nano-range) to exert the requisite properties to function effectively. On the other hand, nanotechnology could be defined as the manipulation of matter through certain physical and/or chemical processes to produce materials that have specific properties which can be used in particular applications. Nanoparticles are particles that have at least one dimension less than 100 nm in size (Jeevanandam *et al*., 2018). Ahmed *et al*. (2016) defined "Nanomaterials" as those particles whose size lies in the dimension area of 1–100 nm. Nanomaterials are found to show enhanced properties based on morphology, size and distribution.

Nanotechnology is no doubt emerging as a vital area of study with its incredible applications in the areas of science, engineering, medicine, catalysis, pharmacy, electrochemistry, sensors, biomedicines, food technology, cosmetics, textile industry, optics, electronics, space industry, mechanics, energy science and optical devices. Nano-photocatalyts have equally gained much attention due to its structural and optical characteristics in the degradation of pollutants.

Zinc oxide and silver Nano-Particles (NPs) have attracted much interest in the research community among metal and metal oxide NPs, owing to their outstanding properties in terms of use in different areas such as antimicrobial, optical and catalytic properties (Espitia *et al*., 2016; Khan *et al*., 2016). ZnO NPs have shown different physical and chemical properties depending on the morphology. ZnO NPs have been synthesized by different methods such as sol–gel method, electrophoretic deposition, laser ablation, hydrothermal methods, electrochemical depositions, co-precipitation, ultrasound, chemical vapor deposition, thermal decomposition, combustion method and microwave-assisted combustion method (Ahmed *et al*., 2016). These physical and chemical methods have major shortcomings such as chemical poisoning and low surface area of the synthesized material. Therefore, any method that is environmentally friendly and that could result to improvement in the surface area of the synthesized ZnO NPs is urgently needed. However, in recent findings, ZnO NPs have also been synthesized by biological method using biological agents as reducing agents (Madhumitha *et al*., 2016 & Ahmed *et al*., 2016). ZnO NPs are non-toxic, semi-conducting materials having good photocatalytic behavior and high transparency. In addition, ZnO NPs produced from biological method have shown remarkable photocatalytic degradation of many dye pollutants like methylene blue, reactive dyes, direct dyes, disperse dyes, methyl orange, basic dyes, azo dyes, rhodamine blue

amongst others (Ghaly *et al*., 2014). Worthy of note is that ZnO NPs have gained special attention due to environmental concerns and it ability to degrade leading water pollutants particularly those in industrial effluents (Bhuyan *et al*., 2015).

Ahmed *et al*. (2015) in a meta-analysis reported the use of plant extract in the green synthesis of photocatalysts. These extracts include those of Ziziphora tenuior (Sadeghi & Gholamhoseinpoor, 2015), Abutilon indicum (Ashokkumar *et al*., 2013), Solanum tricobatum (Logeswari *et al*., 2013), Erythrina indica (Rathi Sre *et al*., 2015), Ocimum tenuiflorum (Logeswari *et al*., 2013), Spirogyra varians (Salari *et al*., 2014), Melia dubia (Ashokkumar *et al*., 2013), leaf extract of Acalypha indica with high antibacterial activities (Krishnaraj *et al*., 2010). Also, extracts of Sesuvium portulacastrum with nanoparticle size ranging from 5 to 20 nm (Nabikhan *et al*., 2010) have been identified as a source for the synthesis of nanoparticles as an alternative to the conventional methods. *Azadirachta indica* (Neem) leaf extract have been studied by Ahmed *et al*. (2016) and reported that the extract plays an important role in synthesis of ZnO NPs functioning as capping and stabilizing agent. They also noted that different capping agents can be used to stabilize ZnO particles imparting different properties, like size and morphology. They further reported that different surfactants have been employed in the synthesis of ZnO NPs, but the challenge with these surfactants is that they are difficult to degrade and are environmentally hazardous. Hence; the need to introduce green capping agents in the synthesis of ZnO NPs becomes imperative. Again it is important to bear in mind that synthesis of NPs is entirely dependent on biochemicals present in the precursor materials such as alkaloids, and others. Actually, the biochemicals present in the neem leaf extract can be a viable alternative.

The 'green' environment friendly methods being talked about in chemical and chemistry technologies are becoming increasingly popular and are much needed now because of the worldwide problems associated with environmental health (Thuesombat *et al*., 2014; Ahmed *et al*., 2016).

In the last ten years or more, researchers have showed interest in biological method to synthesize metal and metal oxide nanoparticles and the development of this biologically stimulated technique is growing as an important branch in the field of nanotechnology and nanoscience (Sharif *et al*., 2017). This so-called green synthesis of nanoparticles is gaining importance and has recently been suggested as potential alternative to physical and chemical methods because it is eco- friendly, non-toxic and safe reagents during the green-synthesis process while the use of Dalbejiya (Neem) leaf extract offers a biological method for the controlled and precise synthesis of several metallic nanoparticles with well-defined various shapes and sizes.

The bio-reduction of zinc ions into respective nanoparticles mediated by Dalbejiya leaf extract is chemically complex but environmentally benign. The role of neem leaf extract as reducing and mediating agent in the biosynthesis of ZnO nanostructures makes it indispensable in green technology (Bhuyan *et al*., 2015). On a general note, plant-extract-based and sodium hydroxide (NaOH)-enhanced simple precipitation processes are the most commonly used procedure in the synthesis of ZnO nanoparticles with NaOH as pH adjuster for the reaction mixture (Vishnukumar *et al.*, 2018).

The wide variability of metabolites present in the Dalbejiya leaf extract have reducing properties or antioxidants that help in the immediate reduction of the zinc ions into nanostructured ZnO photocatalyst. Flavones, ketones, organic acids, amides and aldehydes are the main phytochemicals present in the Dalbejiya leaf extract which acts as bio-reductant out of which flavones, organic acids and quinones are water soluble phytochemicals that are actually responsible for the direct reduction of zinc ions into their respective nanostructures (Prathna *et al*., 2010; Bhuyan *et al*., 2015). Previous studies have further demonstrated that mild heating, followed by subsequent incubation of three types of benzoquinones (namely, cyperoquinone, dietchequinone and remirin) present in neem (mesophyte) leaf extract end up in the activation of quinones which results in particle size reduction (Bhuyan *et al*., 2015). Green synthesis is employed in this research because it is cheap, eco-friendly, and highly efficient method since it does not use toxic precursor as compared with the physical and chemical synthesis approach. This study seeks to synthesize ZnO nanoparticles with an increased surface area through green synthesis.

2.0 MATERIALS AND METHODS

2.1 Materials

Chemical and reagents such as the precursor [Zinc acetate dihydrate [$Zn(CH_3COO)_2$]-$2H_2O$], and sodium hydroxide (NaOH) were of analytical grade as supplied by Panlac Chemicals Nigeria Limited and were used directly without further purification.

Fresh leaves of Dalbejiya (*Azadirachta indica*) were randomly collected from different locations in Gidan Kwano, Bosso Local Government Area, Minna, Niger Sate, Nigeria. The collected leaves were gently washed with tap water and subsequently with de-ionized water, cut into pieces, sun-dried for seven days afterward grinded using plastic mortar and pestle. The resulting powder was stored in an air tight container for subsequent uses.

2.2 Method

Preparation of Dalbejiya Leaves Extract

Thirty gram (30 g) of the powder leaves was weighed into a beaker containing 300 ml de-ionized water. The mixture

was placed for 15 min at 60 °C on a heating mantle. The extract which was allowed to cool at ambient temperature was filtered using Whatman No.1 filter paper. The obtained extract (filtrate) was poured into a bottle and stored in a refrigerator at a temperature of 4 °C for further use. The method of Singh *et al*. (2019) was adopted.

Non-Green Synthesis of Zinc Oxide (ZnO) Nanoparticles

Zinc oxide nanoparticles was synthesized by slightly modifying the method of Bhuyan *et al*. (2015). One molar (1 M) of aqueous sodium hydroxide (NaOH) was prepared by adding 40 g of the crystals in 1000 ml of de-ionized water. To synthesize the non-green ZnO nanoparticles, 20 g of the Zinc acetate [$Zn(CH_3COO)_2$]-$2H_2O$] was added to 60 ml of de-ionized water in a beaker and stirred at 50 rpm for 60 min. The mixture then was divided into three equal volumes and with controlled drops of aqueous NaOH into each beaker, pH values of 8, 10 and 12 were measured using a pH meter. 20 ml of de-ionized water was subsequently added to each of the 3 beakers, stirred rigorously and allowed to settle for 30 min and then decanted after which the same volume of water was repeatedly added twice and decanted. The gel obtained were properly dried in an oven over night at 150 °C and then calcined at 350 °C for 2 h using muffle furnace.

Green Synthesis of Dalbejiya Based Zinc Oxide (ZnO) Nanoparticles

Zinc oxide nanoparticles were bio-synthesized following the method of Bhuyan *et al*. (2015). In the green synthesis of the Dalbejiya based ZnO nanoparticles, 20 g of Zinc acetate was added to 60 ml of de-ionized water in a beaker followed by 30 ml of the Dalbejiya (*Azadirachta indica*) extract and stirred for 60 min at a rotation speed of 50 rpm. The mixture then was divided into three equal volumes and was adjusted to pH 8, 10 and 12 as described in the non-green synthesis. Twenty (20) ml of de-ionized water was subsequently added to each beaker, stirred rigorously and allowed to settle for 30 min. The surfactant was decanted after which the same volume of water was repeatedly added twice and decanted. The gel obtained were properly dried in an oven over night at 150 °C, calcined at 350 °C for 2 h in a muffle furnace, cooled and stored for use.

Characterization of the Green (G) Synthesized and Non-Green (N) Synthesized ZnO Photocatalysts

The morphology, elemental composition, crystallography, Surface area and adsorption bands of the green and non-green synthesized ZnO nanoparticles were comprehensively examined using SEM, EDS, XRD, FT-IR and BET characterization techniques.

Measurement conditions for surface electron microscopy (SEM) and energy dispersive x-ray spectroscopy (EDXS)

About 0.05 mg of the synthesized green and non-green ZnO nanoparticle was sprinkled in a sample holder covered with carbon adhesive tape which was sputter-coated with gold-palladium (Au:Pd; 60:40) using Quorum T15OT for 5 min to the commencement of analysis. The sputter coated samples were characterized using Zeiss Auriga SEM. The secondary electron mode was activated for imaging and a homogeneous region on the sample was identified. The microscope was operated at 5 KeV for imaging with electron high tension (EHT) of 20 KeV detectors for EDS. The illumination angle was adjusted to 150° and the elemental composition of the sample was determined.

Measurement conditions for x-ray diffraction (XRD)

Approximately 1 g each of the green and non-green synthesized ZnO was crushed into powder and then dispersed into a rectangular aluminum sample holder with the aid of a well cleaned spatula. The sample holder containing the sample was clipped into the XRD instrument. Bruker AXS Advance diffractometer with 2θ range of 5 - 75°, a step size of 0.028°, and operating at 45 KV and 40 mA was used to collect the XRD data. Monochromatic copper (Cu) Kαl radiation with a wavelength of 0.154 nm was used as the X-ray source.

Experimental conditions for Brunner-Emmett-Teller (BET)

The analysis for the surface area, pore volume and pore size distribution of the samples was determined by Brunauer-Emmett-Teller technique using a NOVA 4200e surface area and pore analyzer instrument. Around 100 mg each of green and non-green ZnO photocatalysts powder was weighed and degassed by flowing N_2 at 90 °C for 1 h and then held at 350 °C for 2 h. As the temperature is increased, water vapour was adsorbed from the surface and pores of the sample. The sample was then cooled down and weighed again. The instrument uses physical adsorption and capillary condensation of N_2 principles to obtain information about the surface area and porosity of ZnO nanoparticles.

3.0 RESULTS AND DISCUSSION

3.1 Scanning Electron Microscopy (SEM) Analysis

SEM was employed to analyze the structure of nanoparticles that were synthesized. The SEM images in Figure 1 (a–b) show the changes in morphology of ZnO NPs. The photocatalysts formed are fairly spherical in shape and agglomerated tiny rods. However, the agglomeration was less for the green synthesized sample as compared with the non-green synthesized photocatalyst. Similar result was also obtained by Ungula and Dejene (2016).

3.2 Energy Dispersive X-ray Spectroscopy (EDXS) Analysis

EDX analysis (Table 1, Figures 2 and 3) was carried out to determine the elemental composition and stereochemistry

of the synthesized zinc oxide nanoparticles. The EDS spectra in Figure 2 and Figure 3 indicate that the synthesized samples are composed of zinc and oxygen, and the route has pure ZnO phases. Theoretically, expected stoichiometric mass percent of Zn and O are 80.3% and 19.7% (Bari *et al*. 2009). The green synthesized sample showed a closer theoretical value of Zn and O as shown in Table 1. This high purity of the ZnO NPs was further confirmed by XRD spectra. However, some traces of carbon element were found in the sample, which could be attributed to the carbon tape of the sample holder. Similar result was also reported by Gnanasangeetha and Thambwani (2013).

Table 1: Elemental Composition of the modified (G) and unmodified (N) ZnO samples

Photocatalyst	Zn	O	Total (%)
G-ZnO	88.19	11.81	100
N-**ZnO**	91.57	8.43	100

G = Green synthesized, N = Non-green synthesized

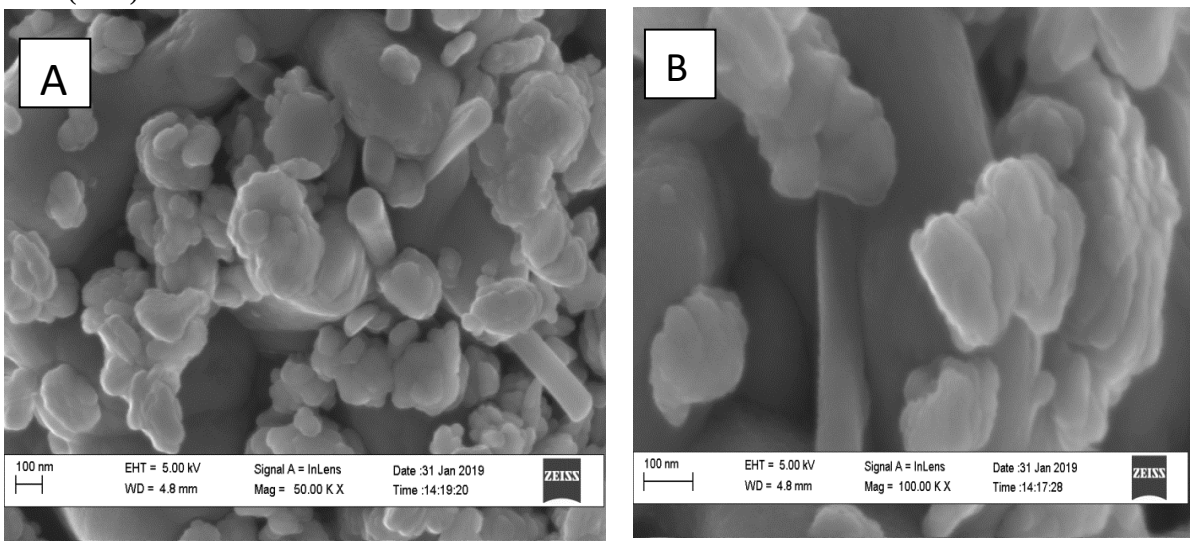

Figure 1: SEM images of (A) Green Synthesized ZnO and (B) Non – Green Synthesized ZnO

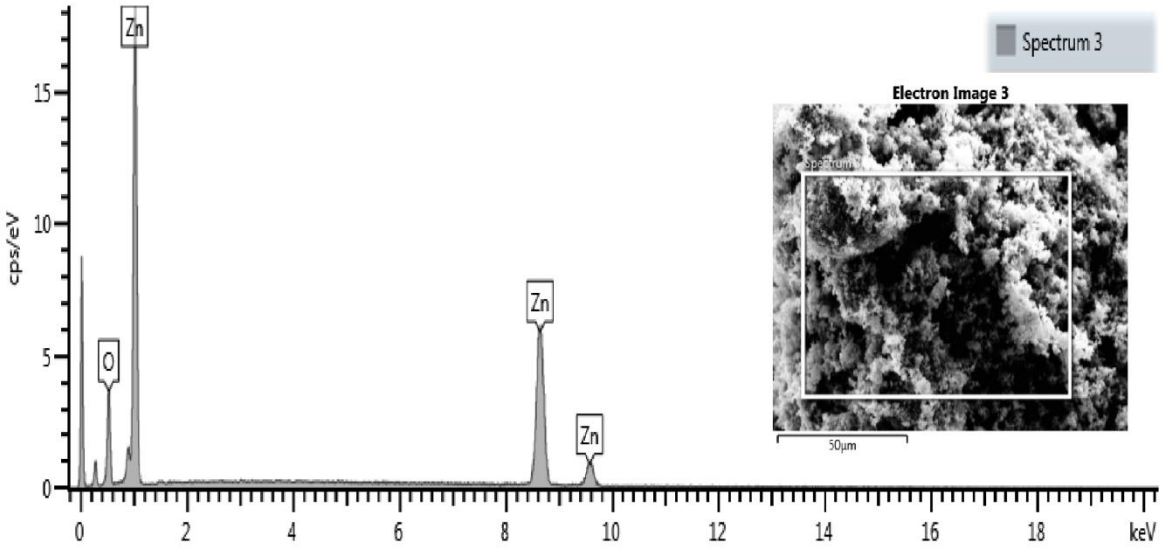

Figure 2: EDX Spectrum of Green synthesized ZnO

DOI: 10.51975/LNDP7232
Journal of the Nigerian Society of Chemical Engineers, 36(1), 2021

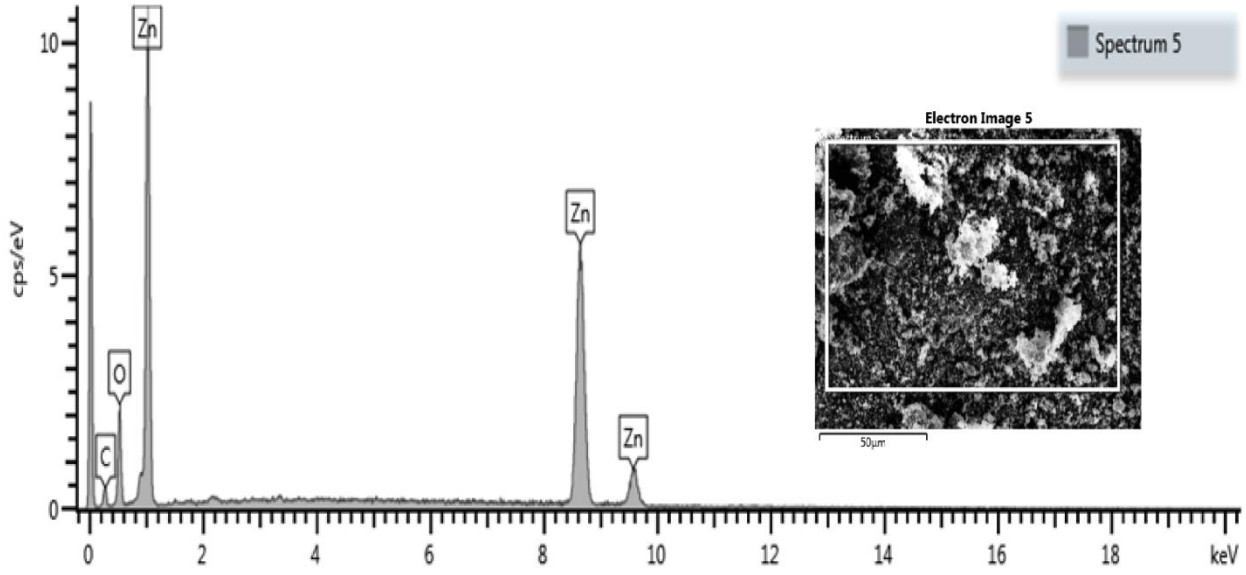

Figure 3: EDX Spectrum of the non-green synthesized ZnO

3.3 X-Ray Diffraction (XRD) Analysis

XRD analysis (Figure 4) was performed to investigate the crystal structure of the synthesized photo catalysts. The XRD patterns of the samples were recorded in the diffraction angle range 5° to 80°. The diffraction peaks at the characteristic planes (1 0 0), (0 0 2), (1 0 1), (1 0 2), (1 1 0), (1 0 3), (1 1 2) and (2 0 1) can be directly indexed to a hexagonal wurtzite crystalline structure of ZnO (Otal *et al.*, 2011). This Wurtzite crystalline structure also matched well with the Joint Committee on Powder Diffraction Studies Standards (JCPDS standard Card No.: 01-036-1451). No other peak was detected, indicating a high phase purity of the samples. The sharp and strong diffraction peaks in the XRD patterns of the zinc oxide nanoparticles synthesized confirm the high crystalline nature of the samples. Figure 4 also shows that the peak intensity increases for the green synthesized ZnO sample, which indicates an increased crystallinity of the modified sample compared to the non-green synthesized ZnO. Similar result was also obtained by Xing *et al.* (2017).

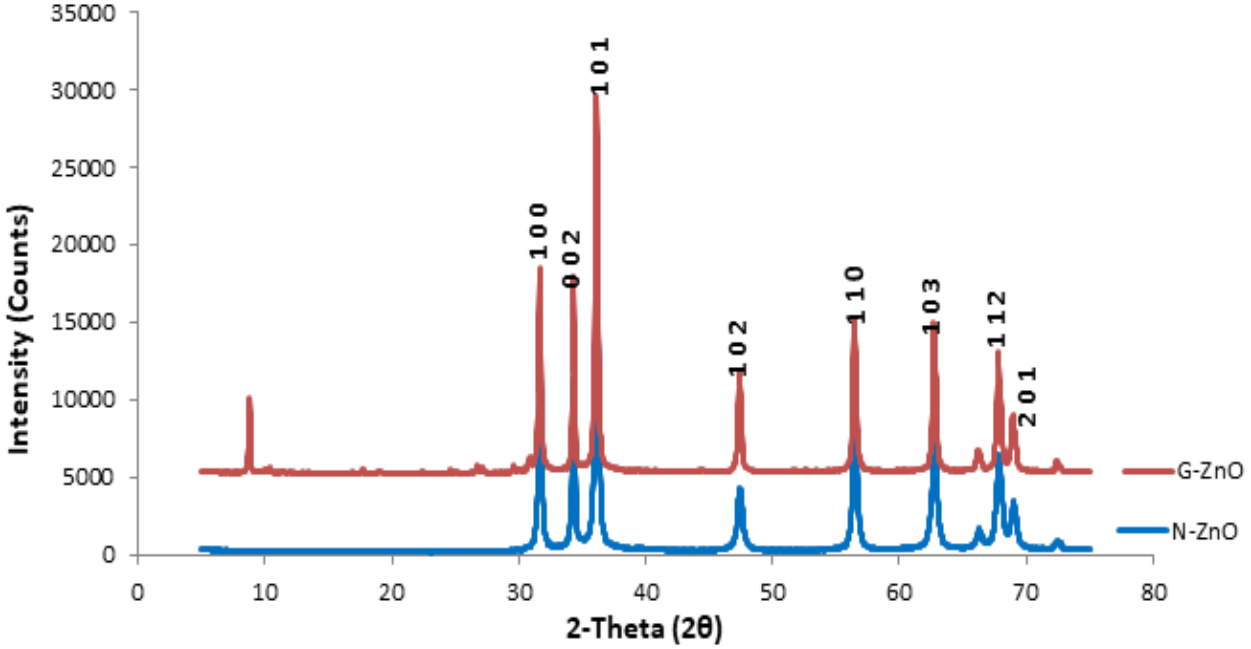

Figure 4: XRD patterns of the green synthesized (G-ZnO) and non-green synthesized (N-ZnO) ZnO samples

3.4. BET Surface Area Analysis

The BET surface area values of the synthesized ZnO nanoparticles are shown in Table 2. The result reveals that the BET surface area of 97.08 m^2/g was obtained for the green synthesized (G-ZnO) sample, an increase of four-folds compared to the value of 23.75 m^2/g for the non-green synthesized (N-ZnO) sample. Based on the surface area values, it can be adduced that neem leaf extract enhanced the surface area of the modified sample.

Table 2: The BET specific surface area, pore volume and pore size of photocatalysts

Photocatalyst	BET Surface Area (m^2/g)	Pore Volume (cm^3/g)	Pore Size (nm)
N-ZnO	23.75	0.01431	2.138
G-ZnO	97.08	0.04949	2.105

3.5 Fourier Transform Infrared (FT-IR) Analysis

FT-IR spectra for the green and non-green synthesized ZnO samples are presented in Figure 5.

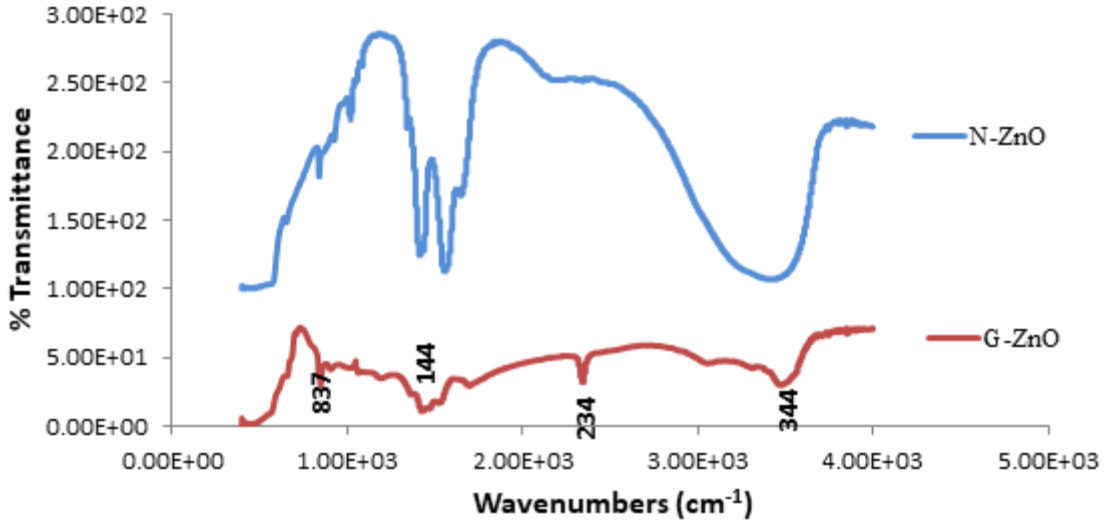

Figure 5: FT-IR spectra of the green synthesized (G-ZnO) and non-green synthesized (N-ZnO) nanoparticles

The peaks at 459 and 400 cm^{-1} identified the bending vibration of Zn-O in the green synthesized and non-green synthesized samples respectively. In addition, the result clearly indicates that –OH stretching around 3042 cm^{-1} and –CH stretching around 2340 cm^{-1} are responsible for strong capping on the green synthesized ZnO nanoparticles. This result matches with the reported result of biosynthesis of ZnO nanoparticles using *Acalypha indica* leaf extract (Gnanasangeetha and Thambwani, 2013).

4.0 CONCLUSION

Zinc oxide nanoparticles have been successfully synthesized via green route, an eco-friendly and inexpensive method for the bio-synthesis of ZnO using aqueous leaf extracts of Dalbejiya (*Azadirachta indica)*. The extracts act as reducing and stabilizing agents for the synthesis of ZnO nanoparticlesThe sharp and strong diffraction peaks in the XRD patterns of the zinc oxide nanoparticles confirm the high crystalline nature of the samples which is a desired property of the material. The EDS result revealed a successful synthesis of ZnO NPs and FT-IR spectra indicates the presence of –OH and –CH stretching which are responsible for strong capping on the green synthesized ZnO NPs. Green-synthesis chemistry of ZnO has fourfold improvement judging by its surface area (97.08 cm^2/g) in relation to the non-green-synthesized ZnO (23.75 $cm^{2/}/g$). From the results obtained, the ZnO nanoparticle is hereby proposed to be applied in the degradation of organic pollutants in wastewater, especially industrial effluents. This therefore, can be gainfully employed in environmental remediation.

ACKNOWLEDGEMENT

The authors wish to acknowledge the support of TETFund in conjunction with Federal University of Technology, Minna for providing 2017 IBRG grant No.: TETFUND/FUTMINNA/2016-2017/6thIBRP/12.

REFERENCES

Ahmed, S., Saifullah, Ahmad, M., Swami, B. L., & Ikram, S. (2016). Green synthesis of silver nanoparticles using Azadirachta indica aqueous leaf extract . *Journal of Radiation Research and Applied Sciences*, *9*(1), 1–7. https://doi.org/10.1016/j.jrras.2015.06.006

Akpan, U.G. & Hameed, B.H. (2009). Parameters

affecting the photocatalytic degradation of dyes using TiO_2-based photocatalysts: A review. *Journal of Hazardous Matrials, 170, 520-529.*

Ashokkumar, S., Ravi, S., & Velmurugan, S. (2013). Green synthesis of silver nanoparticles from Gloriosa superba L. leaf extract and their catalytic activity. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 115, 388-392.

Bari, A. R., Shinde, M. D., Vinita, D. & Patil, L. A. (2009). Effect of Solvents on the Particle Morphology of nanostructured ZnO. *Indian Journal of Pure and Applied Physics*, 47, 24-27.

Bhuyan, T., Mishra, K., Khanuja, M., Prasad, R., & Varma, A. (2015). Biosynthesis of zinc oxide nanoparticles from Azadirachta indica for antibacterial and photocatalytic applications. *Materials Science in Semiconductor Processing*, *32*, 55–61.

Espitia, P.J., Otoni, C.G., Soares, N.F.F. (2016). Zinc oxide nanoparticles for food packaging applications. *Antimicrobial Food Packaging*, 425–431.

Ghaly, A.E., Ananthashankar, R., Althab, M., & Ramakrishnam, V.V. (2014). Production, characterization, and treatment of textile wastewaters: a chritical review. *Journal of Chemical Engineering Process Technology*, 5,182-187.

Gnanasangeetha, D., Thambwani, D.S. (2013). Biogenic production of zinc oxide nanoparticles using Acalypha indica. *Journal of Chemistry, Biology and Physical Sciences*, 1, 238–246.

Jeevanandam, J., Barhoum, A., Chan, Y. S., Dufresne, A., & Danquah, M. K. (2018). Review on nanoparticles and nanostructured materials: History, sources, toxicity and regulations. *Beilstein Journal of Nanotechnology*, *9*, 1050–1074.

Khan, S.T., Musarrat, J., Al-Khedhairy, A.A. (2016). Countering drug resistance, infectious diseases, and sepsis using metal and metal oxides nanoparticles: current status. *Colloids and Surfaces B: Biointerfaces*, 146, 70–83.

Krishnaraj, C., Jagan, E.G., Rajasekar, S., Selvakumar, P., Kalaichelvan, P.T., & Mohan, N. (2010). Synthesis of silver nanoparticles using Acalypha indica leaf extracts and its antibacterial activity against water borne pathogens. *Colloids and Surfaces B: Biointerfaces*, 76, 50-56.

Logeswari, P., Silambarasan, S., & Abraham, J. (2013). Ecofriendly synthesis of silver nanoparticles from commercially plant powders and their antibacterial properties. *Sciencia Iranica*, 20, 1049-1059

Madhumitha, G., Elango, G., & Roopan, S.M. (2016). Biotechnological aspects of ZnO nanoparticles: overview on synthesis and its applications, *Appl. Microbiol. Biotechnol*., 100, 571–581.

Otal, E.H., Yoon, S., Aguirre, M., Weidenkaff, A. (2011). Metastability of heavy lanthanides in the ZnO wurtzite structure. *Journal of Alloys and Compounds*, 509, 364-366.

Prathna, T.C., Mathew, L. Chandrasekaran, N., Raichur, A.M. & Mukherjee, A. (2010). Biomimetic synthesis of nanoparticles: science, technology & applicability, Biomimetics Learning from Nature, (Chapter1).

Rathi Sre, P.R., Reka, M., Poovazhagi, R., Arul Kumar, M., & Murugesan, K. (2015). Antibacterial and cytotoxic effect of biologically synthesized silver nanoparticles using aqueous root extract of Erythrina indica lam. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 135, 1137-1144.

Salari, Z., Danafar, F., Dabaghi, S., & Ataei, S.A. (2014). Sustainable synthesis of silver nanoparticles using macroalgae Spirogyra varians and analysis of their antibacterial activity. *Journal of Saudi Chemical Society*, 20, 459-464.

Sharif, M.M., Shah, F.-H. Butt, M.S. & Sharif, H.R. (2017). Role of nanotechnology in enhancing bioavailability and delivery of dietary factors. *Nutrient Deliv*ery, 587–618.

Singh, A., Neelam, & Kaushik, M. (2019). Physicochemical investigations of zinc oxide nanoparticles synthesized from Azadirachta Indica (Neem)leaf extract and their interaction with Calf-Thymus DNA. *Results in Physics*, *13*, 1–9.

Thuesombat, P., Hannongbua, S., Akasit, S., & Chadchawan, S. (2014). Ecotoxicology and environmental safety effect of silver nanoparticles on rice (Oryza sativa L. cv. KDML 105) seed germination and seedling growth. *Ecotoxicology and Environmental Safety*, 104, 302-309.

Ungula, J. & Dejene, B.F. (2016). Effect of solvent medium on the structural, morphological and optical properties of ZnO nanoparticles synthesized by the sol–gel method. *Physica B*, 480, 26–30.

Vishnukumar, P., Vivekanandhan, S., Misra, M. & Mohanty, A.K. (2018). Recent advances andemerging opportunities in phytochemical synthesis of ZnO nanostructures. *Materials Science in Semiconductor Processing*, 80, 143–161.

Xing, Z., Chen, Y., Liu, C., Yang, J., Xu, J., Situ, Y. & Huang, H. (2017). Synthesis of core-shell ZnO/oxygen doped g-C3N4 visible light driven photocatalyst via hydrothermal method. *Journal of Alloys and Compounds*, 708, 853-861.