# Microwave assisted wet chemical synthesis and characterizations of ZnO nanoflowers for optoelectronic applications

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**Abstract**

In the present work, zinc oxide NFs (NFS) were synthesized by one step microwave-assisted wet chemical process under the amalgamation of 30 mM Zinc nitrate hexahydrate and Hexamethylene-tetra-amine growth solution. The structural and crystallinity of the as grown ZnO NFs were studied by X-ray diffraction examinations. The blossoms-like morphology of prepared of ZnO nanoparticle was verified by FESEM and it shows the approximate size of nanoparticle which is about 18 nm. The optical characteristics of as grown ZnO nanoparticles were examined by absorption spectra UV-visible range. The significant peak of absorption spectra is seen near 348 nm wavelength because of ZnO NFs which explains the monodispersion behavior of nanoparticles. Tauc's relation was used to calculate the optical band gap value of ZnO NFs. The calculated value is 3.75 eV which is greater than pure ZnO bang gap energy (3.51 eV) and showing red shift in energy level. The disorder of the prepared ZnO NFs were characterized using calculating Urbach energy by fitting the linear portion of logarithmic variation curve of absorption coefficient with photon energy. This behavior of as grown ZnO nanoparticles explains the potential and suitability of these materials to be used for optoelectronic applications.

**Keywords:** zinc-oxide, nanostructures, microwave, hydrothermal, NFs, characterization

## 1. Introduction

Over the last few years, there has been an expanding interest for the advancement of nanosized semiconductors because of their critical electrical and optical features which are profoundly helpful in creating nanoscaled optoelectronic and electronic appliances [1]. Among different semiconducting materials, zinc oxide (ZnO) is a promising electronic and photonic material with wide energy band of 3.37 eV and a high binding energy (60 meV) at atmospheric condition [2]. The nanostructures (NSs) of ZnO are potential material classification to investigate due to their affluence of NSs development, assorted morphologies other than being a significant multifunctional material displaying distinguished optoelectronics features much needed for diverse appliances like sensors, catalysts, emitters and biomedical agents [3].

There are various methods to produce ZnO NSs which may follow one of the two general technique that is, aqueous method and vapor method [4]. Out of these, aqueous method is more suitable method because of the several advantages like economical, easiness to grow, low temperature and high purity [5]. Hydrothermal method is improvised form of wet chemical method which provides improved synthesis of NSs because it has low aggregation, narrow particle dispersion and two step technique (seeding and growth) [6][7]. This method also allow formation of pure NSs with excellent morphologies and controlled size [8]. Over the last few years, the microwave heating is more attractive method instead of regular heating for the growth of NSs. The microwave assisted growth is very fast and single step process for growth of NSs. Microwave method possesses uniform and controlled heating followed by minimum power consumption. Several literatures are available on the development of ZnO NSs by microwave assisted hydrothermal techniques [9] but limited work has been done on the impact of synthesis parameters on the characteristics of grown NSs [10].

The present work deals with the preparation of flower shaped ZnO nanoparticles using microwave assisted hydrothermal phenomenon. This work deals with the descriptive analysis of the preparation of the ZnO NFs as function of microwave power and synthesis time. A flower shape of ZnO was formed by the combination of different nanopetals and nanorods due to microwave heating of prepared growth solution. The prepared nanoparticles possess good crystalline structure and excellent optical properties which is needed for optoelectronic applications. The micro-structural lattice disorder was assessed by the calculation of Urbach energy and their value proves the existence of disorder in developed material.

## 2. Materials and methodology

Zinc-oxide nanoparticles were prepared by microwave-assisted hydrothermal technique using hexamethylene-tetraamine (HMTA) and zinc nitrate hexahydrate (ZNH) in deionized water. A ethanol solution was used for cleaning of the prepared nanoparticles. For the growth of ZnO NSs, 30 mM of growth solution was prepared by mixing equimolar proportion of HMTA and ZNH in deionized water. A 30 mM of ZNH was dissolve in 300 ml aqueous deionized water solution and then mixed with the help of magnetic stirrer for 30 minutes and 30 mM of HMTA was also dissolve and prepared 300 ml aqueous deionized water solution by magnetic stirring for 30 minutes. Now the prepared HMTA solution was mix with the ZNH solution in dropwise manner under vigorous stirring for 30 minutes. The final solution was stirred further for 40 minutes which allow proper amalgamation of ZNH and HMTA in ethanol. The final solution was kept sealed at the atmospheric condition for 15 minutes and then placed inside a domestic microwave (make-Samsung-QW71X, frequency 2.45 GHz, maximum power 1600 W) to irradiate the precursor solution for 5 minutes at microwave power set of 1000 W. The microwave irradiation causes the

growth of ZnO NFs in the prepared precursor mixture since photon energy of microwave is respectably low and simply impacting kinetic atomic excitation, in this manner $\{Zn(NH_3)_4^{2+}\}$ and OH- available in the solution begun creating ZnO NFs. After microwave treatment, the resulting solution was allowed to cool at atmospheric condition and then solution was further centrifuge for better filtration of the precipitate. The precipitate was then clean with ethanol and deionized water solution several time for removal of contaminants and by-products. The resulting ZnO nanoparticles were dried in hot air oven for 4 hours at 70°C. The ZnO nanoparticles are left to the atmospheric condition for few hours due to which zinc hydroxide is fully transformed into a ZnO crystal by complete drying. The complete procedure of preparation of ZnO nanoparticle is illustrated in Fig. 1.

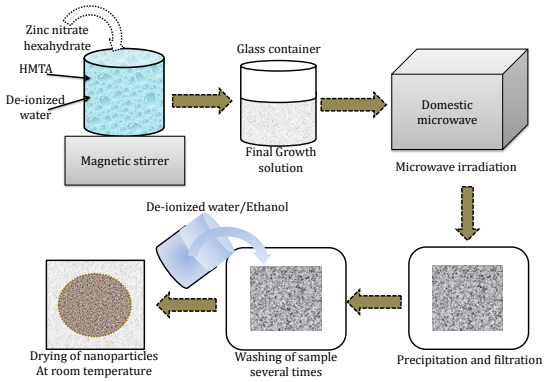


Fig. 1. Stepwise illustration of synthesis of ZnO nanoparticles via microwave assisted hydrothermal route

## 3. Results and discussions

### 3.1 *X-ray diffraction*

X-ray diffraction technique is used for the study of grown structure and their crystal behavior using a X-ray diffractometer containing Cu-Kα radiation. The XRD peaks of as prepared ZnO NSs are illustrated in fig. 2. The hexagonal wurtzite phase of ZnO NSs was verified by the XRD graph. The developed structure is a zincite crystal having chemical formula $Zn_2O_2$ which has hexagonal crystal system of space group P63 m c and space group number 186. The crystal parameters of developed ZnO are a=b=3.25, c=5.20 and α=β= 90°; γ=120°. ZnO nanoparticles developed on planes having (hkl) values (100), (002), (101), (102), (110), (103), (200), (112) and (201) indexed to angular position of 31.52°, 34.32°, 36.21°, 47.46, 56.49°, 62.89°, 66.28°, 67.94°, 69.10° and 72.42° respectively are in match with the JCPDS database No: 36-1461. Few more peaks of ZnO nanoparticles were seen which is analyzed further and found that the other compound of ZnO were also developed which has Wuelfingite crystal having chemical formula $Zn_4O_8$. This crystal system is Orthorhombic having space group P 21 21 21 of space group number 19 with the crystal parameters a=4.92, b=5.16, c=8.53 A° and α=β=γ=90° were seen. The developed nanoparticles on the planes containing (hkl) value (111), (102), (112), (020), (201), (120), (121), (211), (202), (122), (212), (114), (221), (031), (301), (131), (124) and (302) are indexed to angular position of 27.12°, 27.65°, 32.73°,34.74°, 38.03°, 39.4°, 40.85°, 42.01°, 42.38°, 44.97°, 46.04°, 49.81°, 52.46°, 54.37°, 57.14°, 57.75°, 59.22° and 60.42° respectively as matched with the JCPDS database No-96-101-1224. These are basically anharmonic thermal vibrations in ZnO due to the microwave assisted hydrothermal synthesis technique.

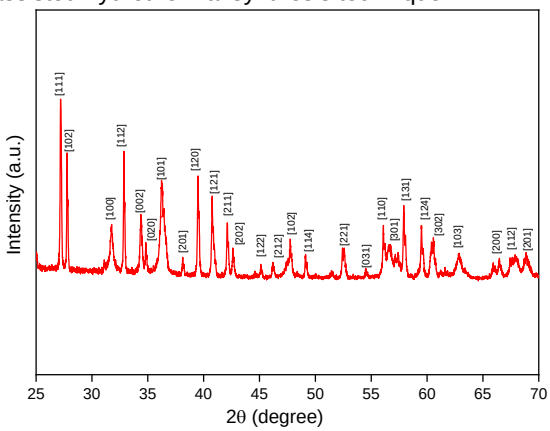


Fig. 2. XRD spectra of prepared ZnO NFs

The diameter of prepared ZnO NFs was derived from Debye-Scherrer expression [11];

$$D = \frac{K\lambda}{\beta_D cos\theta}$$

Where, K is Scherrer's constant (generally K= 0.9), $\lambda$ is the wavelength of X-rays, $\theta$ is the Bragg diffraction angle, and $\beta$ is the FWHM (full width at half-maximum) of the diffraction spectrum which is used to calculate average size of particle along (101) plane at 36.21° by applying Scherrer's relation. So by this method the average value of particle size is approximately 17 nm. W-H plot of the diffraction peak was used to calculate the value of strain because of imperfection in the crystal using the Williamson–Hall expression [11]:

$$\varepsilon = \frac{(\beta_{hkl})}{4\ tan\theta}$$

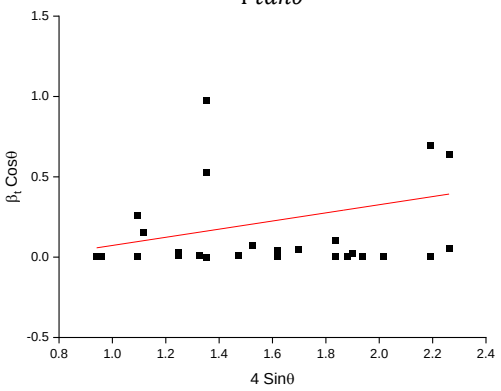


Fig. 3. W-H plot of as synthesized crystalline ZnO nanoparticles

The graphical representation of variation of (4 sinθ) and ($\beta_t$ cosθ) corresponding to x-axis and y-axis respectively is called as W-H plot as depicted in the fig. 3. The slope of the graph gives the value of strain which is observed to be equal to $5.03698 \times 10^{-4}$ and the intercept on the y-axis will give the value of crystallite size which is approximately equal to 16.82 nm. The value of "m" represent gradient of the line, so it will be the value of the strain "ε". Finally, the value of crystallites size will be calculated from the y-

intercept "$\frac{K\lambda}{D}$". From the W-H plot, strain is 5.03698 × $10^{-4}$ and crystallite size is $16.82\,nm$. The value of stress in the system can be calculated by applying Hooke's law i.e., $\sigma = E\varepsilon$, where E is the bulk Young's modulus which is equal to 1.46×$10^{10}$ N/$m^2$, ε is the strain in the particle and σ is the corresponding stress in the system. Thus, the strain (ε) and stress (σ) of the ZnO nanoparticles were found to be approximately 5.03698 × $10^{-5}$ and 7.35 MPa.

### 3.2 *Morphological study of synthesized ZnO nanoparticles*

The morphological characterization of as synthesized ZnO nanoparticles was done by FESEM model-Supra 55 (make-Carl Zeiss, Germany) at varied magnifications. From FESEM image (fig. 4), it was seen that the developed nanoparticles have flowers like nanostructure as illustrated with the enlarged view in inset at magnification of 60 KX and 200 nm size. This micrograph confirms the formation of ZnO NFs.

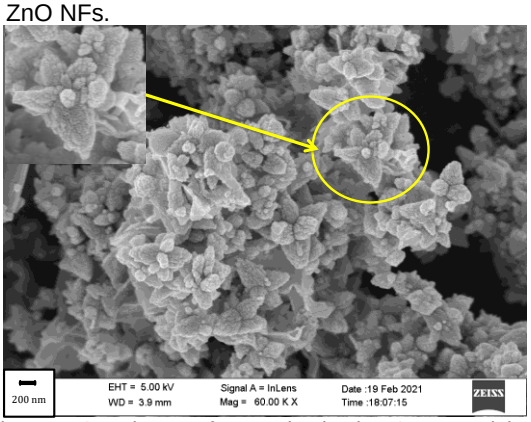


Fig. 4. FESEM image of as synthesized ZnO NFs and their enlarged view as depicted in inset

The micrograph substantiates the blossom-like structure to the ZnO NSs, and all the petals of the blossoms showing part of carve. The flower shape of ZnO nanoparticles was developed due to the microwave heating followed by cooling to the room temperature by combining the different nanopetals and nanorods. The calculation of size of ZnO NSs was done by analysing FESEM image using imageJ software and the size of the NFs are found to be in the range of 18 nm which shows conformity with the calculated particle size by XRD peaks Scherrer expression.

### 3.3 *Optical characterization by Absorption spectra*

The overall property of the ZnO NSs significantly relies upon the crystallite size. In this way, the analysis and development of size of ZnO NSs as a semiconductor material turns out to be fundamental to investigate the materials properties. The most common method to understand the optical features of the ZnO NFs is analyzing the absorption spectra using UV-vis spectrophotometer (model-Agilent Cary 5000) as depicted in the fig. 5. A sharp variation in the absorption spectra is observed near the wavelength value of 348 nm which shows the presence of ZnO nanoparticles. This wavelength value is lower than the wavelength (353 nm) corresponding to energy band gap value of ZnO ($E_g$ = 3.51 eV). This sharp absorption due to ZnO NFs significantly expresses the monodispersion of the nanoparticles [11]. Finally the Tauc's expression of optical characterization is used for the energy band gap value of the ZnO NFs as [12]:

$$(\alpha h\upsilon)^n = B(h\upsilon - E_g)$$

Where, $E_g$ is the energy band gap, α is an absorption coefficient, hu is called as photon energy, B is a material dependent constant and n represent the type of transition (in this case n = ½ i.e., direct transition). Thus the direct energy band can be calculated by the Tauc's plot as depicted in the fig. 6.

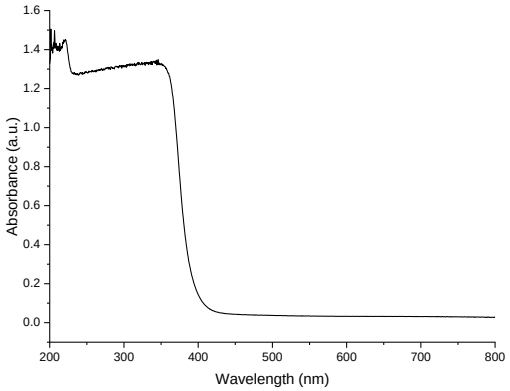


Fig. 5. Absorption spectra of ZnO NFs

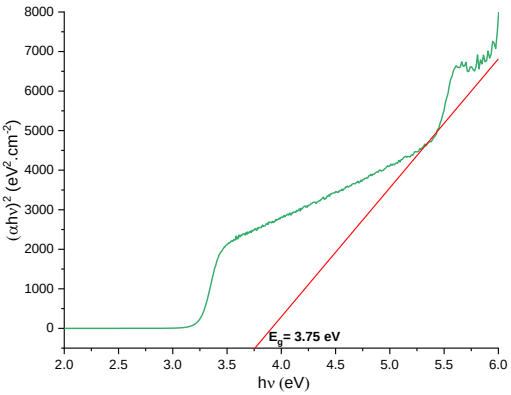


Fig. 6. Band gap calculation of ZnO NFs by Tauc's plot method

The derived value of the energy band is 3.75 eV by using linear fitting of the curve after the linear variation. The value of band gap is differing with pure ZnO by 0.24 eV which may arise due to post annealing in the hot air oven after the microwave treatment. This small increase shows the red shift in wavelength of the resulting material because of quantum confinement which may present due to the imperfections or vacancies possesses in the inter-granular zone creating other energy band to increase the energy level of the ZnO NFs. This behavior of as prepared ZnO nanoparticles indicates the potential of the material to be applicable in the optoelectronics fields [13].

### 3.4 *Urbach energy*

To study of the disorderness of the prepared ZnO nanoflwoers, the amount of Urbach energy associated with it, is calculated. The value of an

Urbach enegy deals with the conversion of increased valance band and the localized conduction band. The Urbach energy is also defined as the size of localized state of the band in the energy band [14]. Thus the degree of disorderness of the ZnO nanoparticles can be deduced by the variation in the coefficient of absorption. In the region of ($h\upsilon<E_g$), following expression can be used to define Urbach energy [14];

$$\alpha = \alpha_0 \exp\left\{\frac{h\upsilon}{E_u}\right\}$$

Where, $E_u$ represents the Urbach energy and $\alpha_0$ is a constant. The Urbach energy is calculated from the graph of logarithmic variation of absorption coefficient as a function of wavelength by deducing the reciprocal of the slope of linear region of the graph as depicted in the fig. 7. In this case the value of Urbach energy is 0.34 eV which exhibits the existence of the disorderness in the material which is combined with lattice disorderness of microstructure.

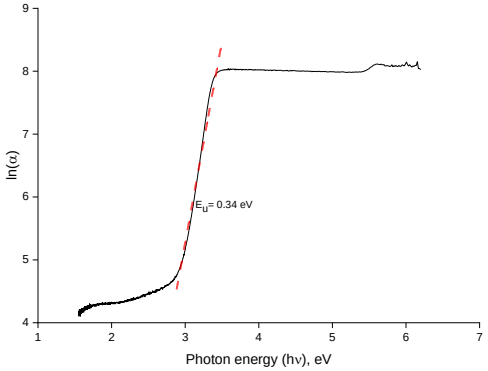


Fig. 7. Demonstration of Urbach energy

## 4. Conclusions

Rapid synthesis of ZnO NFs of a wurtzite phase has been successfully done using microwave assisted hydrothermal synthesis method in small synthesis time of 5 minutes. The characterizations of crystalline structure and morphology of prepared ZnO NFs have been verified by FESEM and XRD analysis. The Scherrer's relation and W-H plot method has been used for the calculation of particle size of the prepared ZnO NFs. The values of particle size from both the methods are found in the range of 16-18 nm. Optical properties of of ZnO NFs were analyzed by UV-vis absorption spectrum. Absorption spectra reveals that the sharp exciton absorbance band near the wavelength 348 nm that shows the validation with the bnad value of pure ZnO at 353 nm wavelength. The corresponding energy band gap value is 3.75 eV which is derived by Tauc's method and shows red shift in the wavelength due to presence of oxygen vacancies. Calculation of Urbach energy of ZnO NFs (Eu=0.34 eV) exhibits the occurrence of micro-structural lattice disorder in the materials. These properties of as prepared ZnO NFs exhibit their potential to be used for the optoelectronic applications such as sensors, emitters, catalysts, active medium and electrodes.

## References


[1] J. Wang, R. Chen, L. Xiang, and S. Komarneni, "Synthesis, properties and applications of ZnO nanomaterials with oxygen vacancies: A review," *Ceramics International*. 2018, doi: 10.1016/j.ceramint.2018.02.013.

[2] T. Blachowicz and A. Ehrmann, "Recent developments in electrospun ZnO nanofibers: A short review," *Journal of Engineered Fibers and Fabrics*. 2020, doi: 10.1177/1558925019899682.

[3] A. Sulciute *et al.*, "ZnO Nanostructures Application in Electrochemistry: Influence of Morphology," *J. Phys. Chem. C*, 2021, doi: 10.1021/acs.jpcc.0c08459.

[4] V. Gerbreders *et al.*, "Hydrothermal synthesis of ZnO nanostructures with controllable morphology change," *CrystEngComm*, 2020, doi: 10.1039/c9ce01556f.

[5] H. D. Cho, D. Y. Kim, and J. K. Lee, "Zno nanorod/graphene hybrid-structures formed on Cu sheet by self-catalyzed vapor-phase transport synthesis," *Nanomaterials*, 2021, doi: 10.3390/nano11020450.

[6] R. S. Rai and V. Bajpai, "Hydrothermally grown ZnO NSs on Bi-Directional woven carbon fiber and effect of synthesis parameters on morphology," *Ceram. Int.*, 2020, doi: 10.1016/j.ceramint.2020.11.180.

[7] D. Kumar, R. S. Rai, and N. K. Singh, "An innovative approach to deposit ultrathin ZnO nanoflakes (2D) through hydrothermal assisted electrochemical discharge deposition and growth method," *Ceram. Int.*, 2020, doi: 10.1016/j.ceramint.2020.07.009.

[8] R. S. Rai and V. Bajpai, "Fabrication of ZnO nanostructures on woven carbon fiber via hydrothermal route and effect of synthesis conditions on morphology," 2019, no. Copen, pp. 1–4.

[9] J. Wojnarowicz, T. Chudoba, and W. Lojkowski, "A review of microwave synthesis of zinc oxide nanomaterials: Reactants, process parameters and morphoslogies," *Nanomaterials*. 2020, doi: 10.3390/nano10061086.

[10] N. Senthilkumar, E. Vivek, M. Shankar, M. Meena, M. Vimalan, and I. V. Potheher, "Synthesis of ZnO nanorods by one step microwave-assisted hydrothermal route for electronic device applications," *J. Mater. Sci. Mater. Electron.*, 2018, doi: 10.1007/s10854-017-8223-5.

[11] K. Ocakoglu, S. A. Mansour, S. Yildirimcan, A. A. Al-Ghamdi, F. El-Tantawy, and F. Yakuphanoglu, "Microwave-assisted hydrothermal synthesis and characterization of ZnO nanorods," *Spectrochim. Acta - Part A Mol. Biomol. Spectrosc.*, vol. 148, pp. 362–368, 2015, doi: 10.1016/j.saa.2015.03.106.

[12] I. Ben Saad, N. Hannachi, T. Roisnel, and F. Hlel, "Optical, UV-Vis spectroscopy studies, electrical and dielectric properties of transition metal-based of the novel organic-inorganic hybrid (C6 H10 N2)(Hg2Cl5)2.3H2O," *J. Adv. Dielectr.*, 2019, doi: 10.1142/S2010135X19500401.

[13] H. H. Azeez, A. A. Barzinjy, and S. M. Hamad, "Structure, synthesis and applications of ZnO nanoparticles: A review," *Jordan Journal of Physics*. 2020, doi: 10.47011/13.2.4.

[14] A. Bougrine, A. El Hichou, M. Addou, J. Ebothé, A. Kachouane, and M. Troyon, "Structural, optical and cathodoluminescence characteristics of undoped and tin-doped ZnO thin films prepared by spray pyrolysis," *Mater. Chem. Phys.*, 2003, doi: 10.1016/S0254-0584(02)00505-9.