# MORPHOLOGICAL AND STRUCTURAL PROPERTIES OF ZnO NANORODS FABRICATED BY MICROWAVE ASSISTED HYDROTHERMAL METHOD

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*In this paper, we present a low-cost and fast zinc oxide (ZnO) nanorods growth method based on hydrothermal processes and microwaves. By field emission scanning electron microscopy (FESEM), two morphologies of fabricated ZnO nanorods were observed, flower-like and needle-like, respectively. The specific crystalline structure of wurtzite together with the preferential growth direction on c-axis was determined by X-ray diffraction, confirmed by Raman measurements. The presence of the peaks corresponding to the planes with the Miller indices (101), (102) and (103) indicates not all the fabricated ZnO nanorods are perfectly perpendicular to the substrate. With diameters in 90 – 650 nm range and 1.5 – 6.5 µm lengths, future investigations are required in order to determine the optimal aspect ratio values for appropriate applications.*

**Keywords**: ZnO, nanorods, hydrothermal method, microwaves

## 1. Introduction

In the introduction to the paper, the author(s) will specify the present stage of the branch researches (by quoting the adequate bibliography) and will specify the purpose of the paper.

Zinc oxide (ZnO) is an n-type semiconductor with wide bandgap of about 3.37 eV at room temperature and large exciton binding energy of 60 meV [1,2]. Because of its important advantages like abundance in nature, low-cost, non-toxicity and high thermal and chemical stability [3,4], it is frequently used in various applications, like solar cells [5], sensing devices [6,7], light emitting diodes (LED) [8] or field-emission devices [9,10]. Moreover, its versatility is responsible for a huge variety of morphologies obtained by chemical vapor deposition (CVD) [11], vapor-liquid-solid growth (VLS) [12], hydrothermal processes or template-based methods [13]. Among these morphologies, nanorods and nanowires are currently intensively studied because of their special properties, suitable for electronic and optoelectronic applications. Due to a slower electron-

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hole recombination rate and big values of surface/volume ratio, ZnO 1D structures are one of the building blocks for future nanoscale applications [14]. Because can be obtained very easy by low-cost methods and are appropriate candidates for different applications [15,16], ZnO nanorods attracted important attention from scientific community. Usually, these kinds of structures are obtained by two-step methods; first step consists in deposition of a polycrystalline ZnO thin layer, followed by the growth of ZnO nanorods by hydrothermal processes. This approach is widely used because can cover large areas and the obtained ZnO nanorods are densely packed and perpendicularly oriented to the substrate [14].

In this paper, we present the fabrication of ZnO nanorods using an easy route based on hydrothermal processes and microwaves. Compared with other hydrothermal based growth techniques, this method has important advantages like low-cost production and swiftness. Structural and morphological characterization of fabricated ZnO nanorods was performed, and the obtained results are similar with hydrothermal based methods ones.

## 2. Experimental

### 2.1 ZnO nanorods synthesis

Zinc oxide (ZnO) nanorods were prepared by a facile microwave assisted hydrothermal method. First, optical glass substrates were cleaned by acetone into an ultrasonic bath for 30 minutes. Second, 5 mmol Zn(NO3)2·6H2O (Sigma Aldrich, reagent grade, 98%) were dissolved in 10 mL deionized water under constant stirring. The pH of the solution was adjusted to 10 using ammonia (NH3). The precursor solution of ZnO nanorods was then transferred into a teflon (PFTE) vial. Afterwards, the glass slides were placed into the solution, in the vial. Microwave assisted reactions were carried out under 5 bar nitrogen (N2) pressure in Milestone Synthwave equipment. The vial was irradiated with microwaves (MW) at 120°C for 60 min. In the end, the glass slides were rinsed with deionized water and dried with compressed air. The associated chemical reactions are displayed below, as follow:

$$Zn(NO_3)_{2(aq)} \leftrightarrow Zn^{2+} + 2NO_3^- \quad (1)$$

$$Zn^{2+} + NH_3 \cdot H_2O \rightarrow \left[Zn(NH_3)_4\right]^{2+} \quad (2)$$

$$\left[Zn(NH_3)_4\right]^{2+} + 2HO^- \leftrightarrow ZnO + NH_3 + H_2O \quad (3)$$

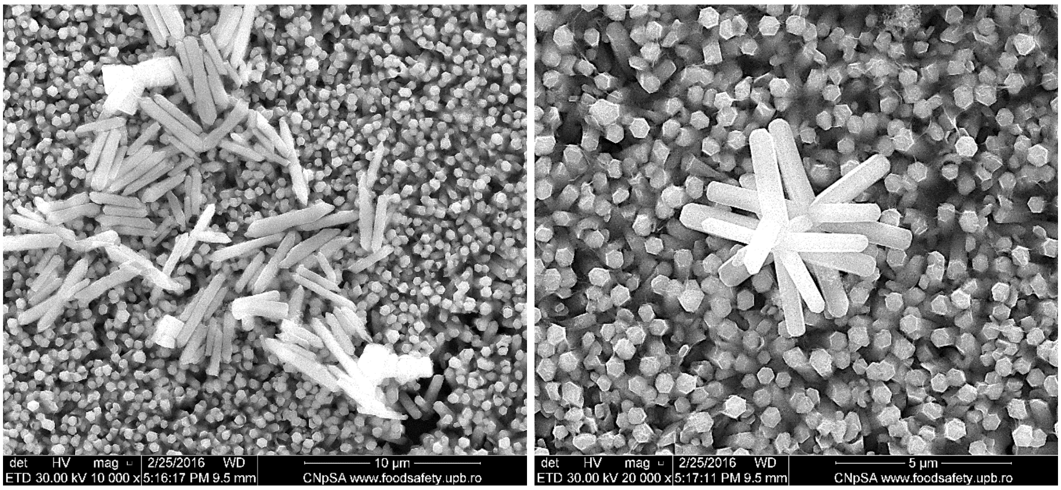
### 2.2 Materials and characterization techniques

Zinc nitrate hexahahydrate reagent grade (Zn(NO3)2, 98%) and ammonium hydroxide solution (NH3, 25%) were purchased from Sigma Aldrich company and were used without further purification. Grazing incidence X-ray diffraction was carried out on a PANalytical Empyrean diffractometer using Cu Kα radiation (λ=1.541874 Å), equipped with a hybrid monochromator 2xGe(220) for Cu and parallel plate collimator on PIXcel3D detector. The scan was made on 2θ axis in the range of 10-80° with an incidence angle of 0.5°, a step size of 0.04° and counting time per step of 3 s. The morphological analysis were performed using a Quanta Inspect F50 scanning electron microscope (SEM) equipped with a field emission gun (FEG) with a resolution of 1.2 nm and coupled with a spectrometer, on sample coated with a gold layer, while for Raman measurements a visible light green laser with an excitation wavelength of 532 nm and 2.33 eV was used.

## 3. Results & discussions

### 3.1Morphological investigations

The synthesized ZnO nanorods were analyzed using ultra-high resolution field emission scanning electron microscopy (FESEM). The FESEM images of fabricated ZnO nanorods are presented in figure 1.



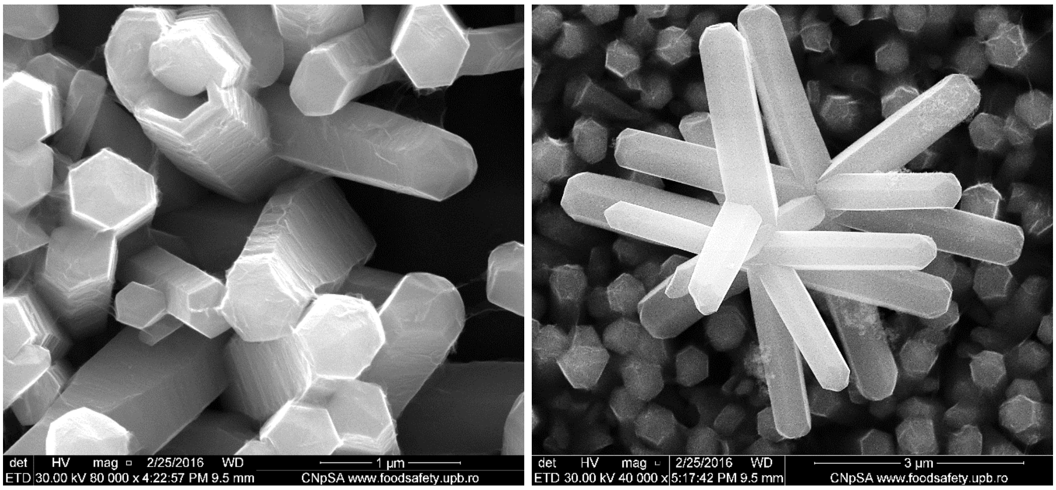
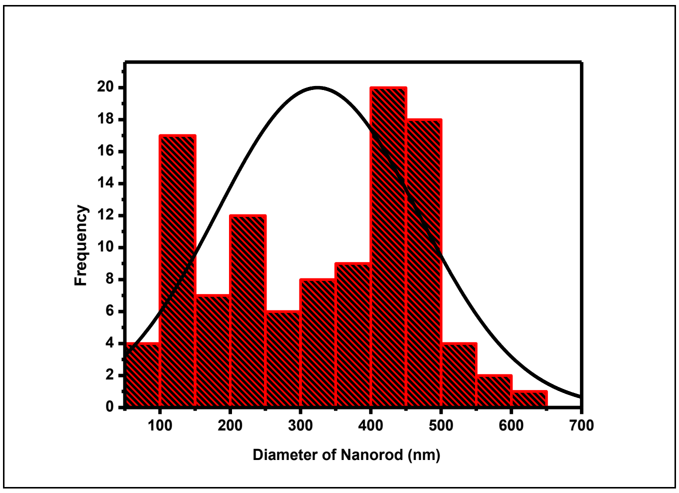



Fig.1. Fabricated ZnO nanorods by microwave assisted hydrothermal method.

By FESEM investigations, a typical wurtzite crystalline structure of prepared ZnO nanorods was revealed together with flower-like and needle-like morphologies. Diameters of the fabricated structures were determined to be in the 90 – 650 nm range, while their length was in 1.5 – 6.5 µm domains. Such obtained values of diameters and lengths of fabricated ZnO nanorods are slightly bigger than usual values obtained by hydrothermal growth methods [14], and new studies are required in order to optimize their dimensions for various electronic or optoelectronic applications. Histograms of diameter and length distributions are presented in figure 2, without taking into account their morphologies.



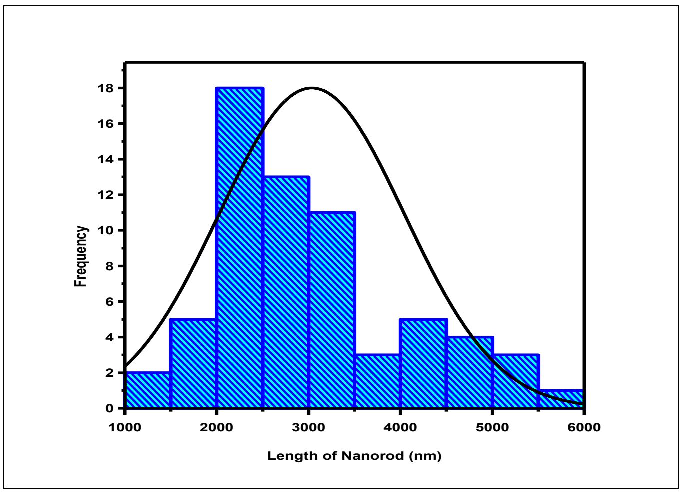



Fig. 2. Histograms of diameter (red) and length (blue) distributions of ZnO nanorods, obtained by microwave assisted hydrothermal method.

### 3.2 Structural characterization

X-ray diffraction pattern of fabricated ZnO nanorods is showed in figure 3. No differences were observed on the obtained structural results between flower-like and needle-like morphologies. The most intense peak located at 34.42° together with the peak at 72.56° proves the preferential growth direction on c-axis. In general, for hydrothermal growth methods compared with vapor-liquid-solid (VLS) or chemical vapor deposition (CVD) techniques, the peaks corresponding to the planes with the Miller indices (101), (102) and (103) can be observed. The presence of these peaks indicates a not well ordered structure or part of those nanorods is not perfect perpendicular to the substrate. In the case of our fabricated samples, taking into account the FESEM investigation, second assumption seems to be valid.

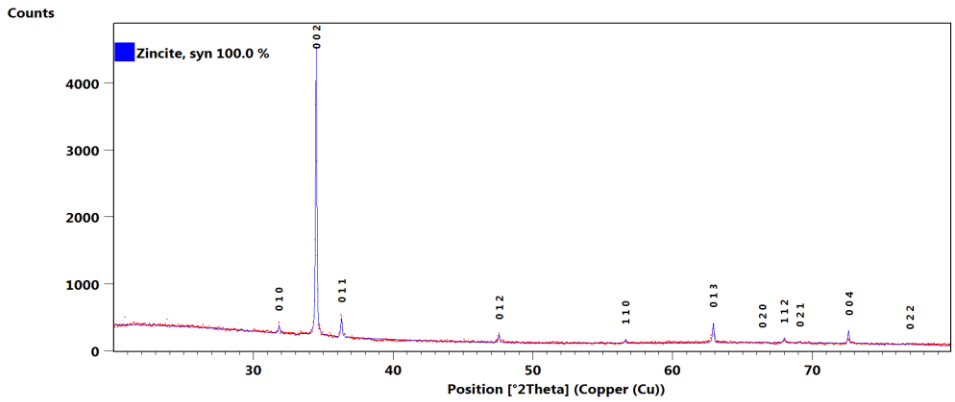



Fig. 3. XRD pattern of ZnO nanorods, obtained by microwave assisted hydrothermal method.

Raman spectra of fabricated ZnO nanorods, drawn using a visible light green laser with an excitation wavelength of 532 nm and 2.33 eV, are depicted in figure 4.

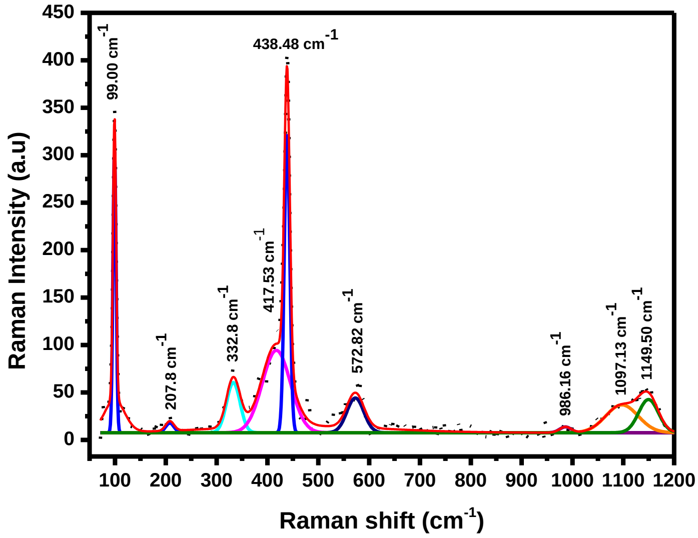



Fig. 4. Raman spectra of ZnO nanorods, obtained by microwave assisted hydrothermal method.

The two dominant peaks at 99.00 cm-1 and at 438.48 cm-1 of the Raman spectra indicate a well-defined crystalline structure, while those at 332.8 cm-1 and 1149.50 cm-1 are related with multi-phonon processes. These results are similar with others suggested by [17] and confirm the preferential growth direction on c-axis.

## 4. Conclusions

ZnO nanorods were obtained by a low-cost and fast microwave assisted hydrothermal method, and were morphological and structural analyzed by field emission scanning electron microscopy (FESEM) and X-ray diffraction, respectively. By FESEM investigations, flower-like and needle-like typical morphologies were revealed. The X-ray diffraction pattern consists, besides the peaks corresponding to (002) and (004) planes associated with wurtzite crystalline structure and the preferential growth direction on c-axis, peaks corresponding to the planes with the Miller indices (101), (102) and (103). The presence of these peaks indicates not all obtained ZnO nanorods are perfectly perpendicular to the substrate. The determined diameters of the fabricated structures were in 90 – 650 nm range, while their length enrolls in the 1.5 – 6.5 µm domains.

## Acknowledgments

Jasim Al-Zanganawee acknowledges the support from the ministry of the Higher Education and Scientific Research of Iraq."

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