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Abstract. Various methods have been introduced to synthesize ZnO nanostructures, however as in most nanomaterial fabrication processes, these methods require sophisticated equipment and relatively high cost. Hydrothermal method has been known as a simple and inexpensive route to produce ZnO nanostructures. Unfortunately, this method takes a long production time in order to produce high quality ZnO hence making it less efficient. In this study, ZnO micro-nano structures have been successfully synthesized via a fast and low wattage microwave-assisted hydrothermal growth. X-ray diffraction and scanning electron microscope characterizations were done on samples. The rapid heating process generated from rotation, friction and collisions of water molecules inside the microwave resulted in faster reaction process compared with conventional hydrothermal method. Due to its time and cost efficient, this method is useful for optimizing the resulted ZnO and its further applications.

1. Introduction

Research in field of nanotechnology and materials is currently growing rapidly all over the world. This is due to nanomaterials have a wide application in various fields such as telecommunications, electronics, computing, energy, environment, agriculture, transportation, medicine, and pharmacy. One of the nano materials that has many applications is the metal oxide nanostructures such as zinc oxide (ZnO). ZnO is known as a semiconductor material with unique physical and chemical properties that are widely used in electronic and optoelectronic devices, such as sensors and solar cells. Not only that, ZnO has also been applied in the fields of medicine such as biomedical imaging, drug and gene carriers, and biosensors [1]. In the field of cosmetics, we can also easily find the content of ZnO in various beauty products such as sunscreen. ZnO can also be used in the absorption of heavy metals [2]. These make ZnO as one of the materials that continue to be studied by researchers.

In general, ZnO can be produced through physical, metallurgical and chemical fabrication processes. The metallurgical process is based on burning zinc ore (Zn). This process is divided into directly and indirectly methods. Direct method involves reducing process of zinc ore through heating with coal such as anthracite followed by oxidation of zinc vapor in the same reactor. Meanwhile, in the indirect process, zinc metal is melted in the furnace and evaporated at a temperature of around 910 °C. The reaction

between zinc vapor and oxygen will form ZnO [3]. The requirement to use a high reaction temperature is one of the weaknesses of this method. ZnO synthesis methods through physical processes include various methods such as high energy ball milling, laser ablation, physical vapor deposition, sputter deposition, electric arc deposition, and ionizing [4]. Most of these physical methods, such as ball milling method and physical vapor deposition are able to produce large amounts of ZnO that can be applied in industrial needs. However, to control the nanostructures produced through this method is relatively more difficult. One of the unique features of ZnO is the variety of nanostructures that can be produced by controlling the synthesis parameters, both the ZnO 1D nano structure (nano rods, needles, helices, ribbons, and rings), 2D (nanoplate / sheets and nanopellets), and 3D (flowers, dandelions , snowflakes and urchin-like) [3].

Synthesis or fabrication of ZnO nanostructures chemically offers a more diverse and most widely used method by researchers. This is because the chemical method is relatively cheaper and simpler and can be done on a laboratory scale. In addition, synthesis control is easier to be done with variations and parameter optimization. But unfortunately this method is difficult to implement on an industrial scale. Some examples of this method are sol-gel, precipitation, colloid, emulsion, solvo thermal and hydrothermal. The sol-gel method is based on changing the precursor molecules into oxide materials via hydrolysis and condensation reactions. The solid material is described from the solution using sol or gel as an intermediate medium at low temperatures [5]. Meanwhile, the precipitation method utilizes reducing agents or precipitating substances such as KOH [6] which react with zinc salts. The resulting precipitate is then washed and calcined at different temperatures to produce different characteristics and morphology of ZnO [4].

Among these methods, the hydrothermal method by heating using an oven or water bath is the method most widely used by researchers. This is due to a simpler process with a relatively lower reaction temperature, low production costs and not using hazardous chemicals [7]. In addition, the control of the synthesis parameters to produce the desired ZnO nano structure is also easier to do. But unfortunately, this method becomes less efficient because of the length of heating time needed. Another alternative method of heating process is using microwave as we done in this current work. This method is capable of conducting volumetric heating processes with fast reaction times and high reaction rates, selectivity and production. Rapid heating process results from rotation, friction and collision of water molecules in the microwave causing faster reaction processes compared to convection heating through ordinary hydrothermal methods [8,9]. This method has the potential to be applied on a large scale with lower production costs, simple and efficient compared to previous methods. The microwave makes it possible to heat the solution without losing energy to heat the entire vessel portion [3].

2. Materials and method

ZnO nanostructures were synthesized using microwave-assisted hydrothermal growth. Precursor solution with concentration of 0.1 M prepared by mixing 5.220 g zinc nitrate tetrahydrate ($Zn(NO_3)_2.4H_2O$) and 2.804 g hexamethylene tetramine (HMT, $C_6H_{12}N_4$) in 200 ml aquades. Prior to synthesis process, ZnO precursor was ultrasonically cleaned for 30 minutes (48 KHz, 8 Watt) and stirred for 60 minutes. It was then introduced into conventional microwave (SHARP R222y, 399 Watt) for 5 minutes at wattage level of 70% or 279.3 Watt. ZnO solution was then centrifuged and the precipitated ZnO deposited at the bottom of centrifuge tube are collected and dried in an oven. ZnO powder sample was characterized using X-ray Diffraction (XRD) Rigaku Miniflex600 30 kV 10 mA Cu K-α and using scanning electron microscope (SEM-JEOL JSM-6510LA) operated at an accelerating voltage of 15kV.

3. Results and discussion

Figure 1 and Table 1 presented the XRD results of synthesized ZnO powder via microwave-assisted hydrothermal method. This results were in good accordance with ZnO ICSD data collection (PDF reference No. 01-075-0576) thus these revealed that the synthesized ZnO sample has a hexagonal crystal structure belong to P63mc space group.

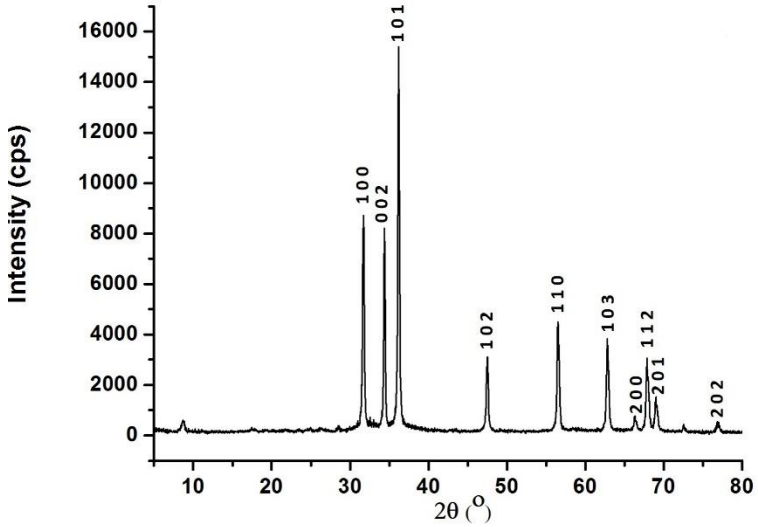

Figure 1. XRD pattern of synthesized ZnO via microwave-assisted hydrothermal growth.

The most prominent peak of ZnO was observed at 2θ of around 36° which represent the growth at *a* nonpolar plane with hkl index 101. This XRD peaks was also similar to previous similar studies in [8,10]. It was then followed by 2θ of around 31° (100 nonpolar *m*-plane) and 34° (002 polar *c*-plane) [7]. Another peaks observed were assigned to different orientation growth of ZnO. There were no other intense impurities peaks observed from the XRD graph. Moreover, high intense, sharp and narrow peaks observed indicated that the synthesized ZnO has a good crystallinity. Furthermore, estimated crystallite size of ZnO was calculated using Scherrer equation [11–13] as presented below:

$$D\ (\mathrm{nm}) = \frac{k\lambda}{\beta Cos\theta} \quad (1)$$

β is full width half maximum (FWHM), θ is half diffraction angle and λ is wavelength used (0.154 nm). *k* is constant and for ZnO material is 0.9. It was found that the calculated crystallite size of synthesized ZnO was in range of around 32 – 48 nm.

Table 1. Detail of XRD analysis and estimated crystallite size of ZnO using Scherrer equation

2θ (°)	d (Å)	Intensity (cps)	FWHM (°)	h k l	Crystallite size (nm)
31.690	2.8212	6219	0.213	1 0 0	38.755
34.374	2.6069	5951	0.173	0 0 2	48.048
36.181	2.4807	10964	0.210	1 0 1	39.782
47.468	1.9138	2487	0.201	1 0 2	43.159
56.484	1.62785	3463	0.247	1 1 0	36.495
62.772	1.47905	2901	0.253	1 0 3	36.768
66.322	1.40823	447	0.252	2 0 0	37.643
67.822	1.38070	2256	0.276	1 1 2	34.670
68.995	1.36006	1089	0.231	2 0 1	41.713
76.80	1.2401	310	0.31	2 0 2	32.687

SEM images of the synthesized ZnO structures is presented in Figure 2. It can be seen from the SEM images, especially from Figure 2(b) that the resulted ZnO has hexagonal rod structures with diameter of several hundred nanometers. However, it can also be observed that the uniformity and purity of the

sample are still low. Agglomerated structures of ZnO were seen together with the rod structures. Several parameters during synthesis process are needed to be optimized in order to produce a better structure of ZnO nanorods. This result was similar to previous work report in [10] where the nanorod structure was produced. Hasanpoor *et. al* [8] also reported the synthesis of ZnO nanoparticles via microwave irradiation and resulted in the production of fine needle and flower-shaped ZnO. However, longer synthesis time of 10 – 15 minutes and higher microwave power of 540 and 680 were used in their study.

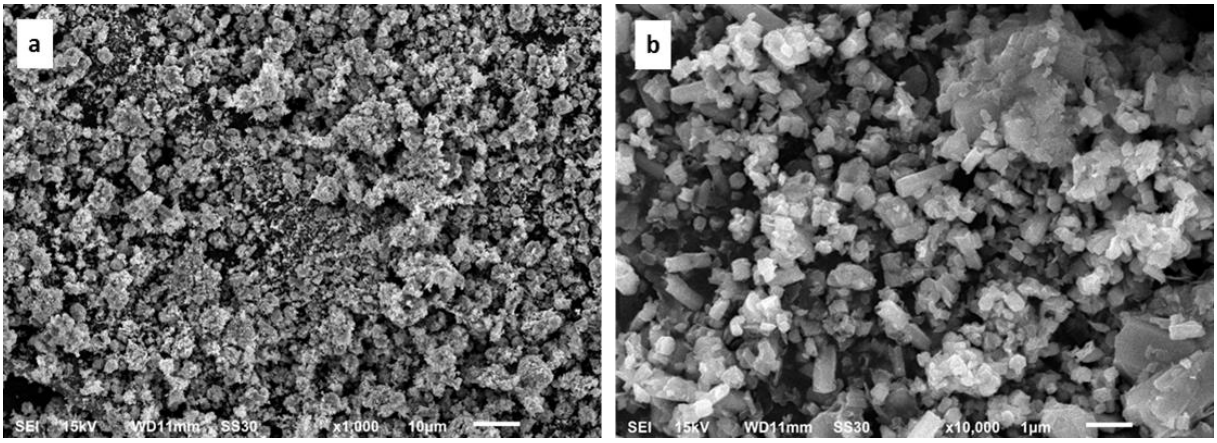

Figure 2. SEM images of the synthesized ZnO with different magnification.

As compared to our similar previous study [7] using conventional heating method by oven, this current study offers time efficient procedure to produce ZnO micro-nanorod structures. Ultra-fast heating process using microwave irradiation was explained resulted from dipolar polarization of water molecules and the ionic conduction of dissolved chemicals [9], in this case zinc nitrate and hexamethylene tetramine as ZnO precursor. Moreover, synthesis process using conventional heating process was explained by convection or conduction so the sample needs longer time to achieve the desired temperature and resulted in in homogenous temperature distribution [10].

4. Conclusion

Hexagonal ZnO micro-nanorod structures were successfully synthesized using an ultrafast microwave-assisted hydrothermal method at low wattage of 279.3 Watt. Structural study using XRD analysis revealed that the synthesized ZnO has a good crystallinity with hexagonal crystal structure and estimated crystallite size of around 32 – 48 nm. Meanwhile the SEM study of the sample showed the production of dense ZnO micro-nanorod structures along with agglomerated structures. Rapid heating process results from rotation, friction and collision of water molecules in the microwave causing faster reaction processes compared to convection heating through ordinary hydrothermal methods. This resulted in faster reaction process to produce ZnO. However, optimization of synthesis parameters is necessary in order to produce a better ZnO structures with higher purity and uniformity.

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