Synthesis and characterization of ZnO nanorods prepared using microwave-assisted hydrothermal method

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Synthesis and characterization of ZnO nanorods prepared using microwave-assisted hydrothermal method

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Abstract. ZnO is one of the most studied semiconductor materials for many applications; however, the synthesis of one-dimensional ZnO nanostructures by a simple and low-cost method in a short time is still a big challenge. The hydrothermal method is a simple way to produce nanostructures but the process is usually slow. However, the reaction can be accelerated using microwaves. This study aims to grow ZnO nanorods were on the glass substrates using ultrasonic spray pyrolysis and microwave-assisted hydrothermal methods. Our goal was to investigate the effect of the concentration of the growth solution containing equimolar amounts of hexamethyelenentetramine and zinc nitrate tetrahydrate (0.05, 0.1, and 0.15 M) on the morphology and structural and optical properties of the ZnO nanorods. Scanning electron microscopy, X-ray diffraction, and ultraviolet (UV)-visible spectroscopy studies demonstrated that an increase in the concentration of the growth solution results in an increase in the lattice parameters, unit-cell volume, crystallite size, density, and diameter of the nanorods. In addition, increasing the precursor concentrations improves the optical absorbance in the UV region and leads to a slight increase in the bandgap energy (from 3.20 to 3.22 eV).

Keywords: semiconductor, ZnO, nanorods, hydrothermal, microwave

1. Introduction

Zinc oxide (ZnO) is one of the most widely studied semiconductor materials for various applications, such as light-emitting diodes [1], photodetectors [2], photocatalysis [3], and sensors. Several forms of ZnO nanostructures, such as nanodots, nanorods, nanowires, nanobelts, nanotubes, and nanobridges have been prepared. Among these, nanorods have been extensively studied owing to its high surface area and ease of preparation. Although great progress has been made, synthesizing one-dimensional ZnO nanostructures using a simple and low-cost method in a short time is still a big challenge. Physical methods, such as chemical vapor deposition, sputtering, and pulsed laser deposition, require complex systems involving high temperatures and a vacuum]. On the other hand, chemical deposition processes, such as hydrothermal methods, are regarded as more practical techniques [4] because they do not require complicated instruments or involve complicated processes. However, long reaction times are needed to grow ZnO structures, and therefore, microwave-assisted hydrothermal methods have been recently introduced for this purpose as they enable high growth rates and lead to high-quality nanostructures [5]. Herein, we synthesized ZnO nanorods on a glass substrate by a two-step process involving the seeding and growth of the nanostructures using microwave-assisted

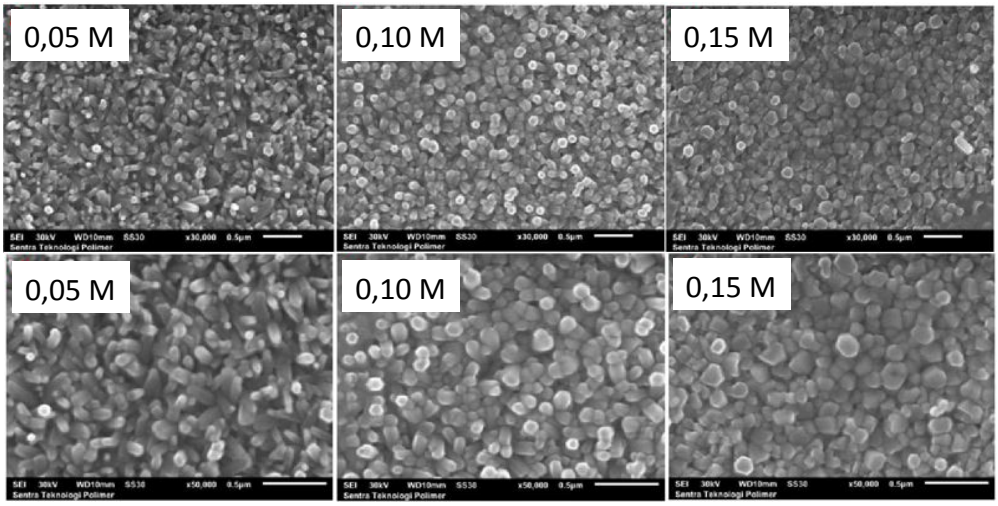

Figure 1. SEM images of the ZnO nanorods prepared herein.

hydrothermal method. Our goal was to investigate the influence of the precursor solution on the morphological, microstructural, and optical properties of the ZnO nanorods.

2. Experiments

In general, the synthesis of ZnO nanorods consists of a seeding process via ultrasonic spray pyrolysis and a growth process via microwave-assisted hydrothermal method. Herein, the seed solution consisted of 0.2 M zinc acetate dihydrate ($Zn(CH_3COO)_2.2H_2O$) in deionized water, which were placed in a container in the nebulizer instrument and vibrated using 1.65 MHz ultrasonic waves. The fine sprays were directed onto the heated glass substrates for 15 min. at 450 °C on a hot plate. The substrates were then annealed at the same temperature for 60 min. The growth solution consisted of equimolar amounts of zinc nitrate tetrahydrate ($Zn(NO_3)_2.4H_2O$) and hexamethylenetetramine ($C_6H_{12}N_4$) at three different concentrations, namely, 0.05, 0.10, and 0.15 M. The glass substrate containing the ZnO seeds was soaked into a glass bottle containing the growth solutions and heated by 240-W microwaves for ten minutes. After completion, the substrates were removed; rinsed using deionized water, and dried with hot air.

Structural characterization was performed using an X-ray diffractometer (Rigaku SmartLab 3kV with CuKα radiation 1.541862 Å), morphological studies were carried out using a JSM-6510LA scanning electron microscope, and the optical properties were determined by recording the absorption spectra on a Thermo Fisher Scientific Genesys 10S Ultraviolet–Visible spectrometer.

3. Results and discussion

3.1. Morphological properties

The surface morphology of the obtained ZnO nanorods is shown in figure 1, where hexagonal nanostructures with different diameters can be observed. In general, the SEM images show that increasing the concentration of the growth solution increases the diameter of the ZnO nanorods. The diameters of the ZnO structures prepared at 0.05 M concentration, were relatively small (89–183 nm) and inhomogeneous, whereas those of the samples prepared at 0.1 and 0.15 M were larger, namely, 91–191 and 118–216 nm, respectively. In addition, the ZnO nanorods were short and relatively transparent. In our previous study, we obtained white ZnO nanorods with a height of more than 1.5 μm [6]. This difference may be due to the low microwave power used herein (240 W). In previous studies, ZnO nanorods longer than 1 μm were prepared using a 750-W microwave power for 20 minutes [7], a 1600-W power for 45 minutes [8], or 1100 W for 20 seconds [9].

The water-based growth solution is basically a microwave absorbent material. The electrical components of electromagnetic waves cause heating through two mechanisms, namely, dipole

Table 1. Microstructural data of the ZnO nanorods.

Concentration	2θ	a=b	c	Volume	Interplanar spacing	FWHM	Crystallite size
		(Å)	(Å)	(Å^3)	(Å)		(nm)
0.05 M	34.36	3.249	5.206	47.672	2.61	0.307	26.8
0.10 M	34.34	3.251	5.208	47.678	2.61	0.273	33.8
0.15 M	34.38	3.251	5.208	47.681	2.61	0.212	42.6

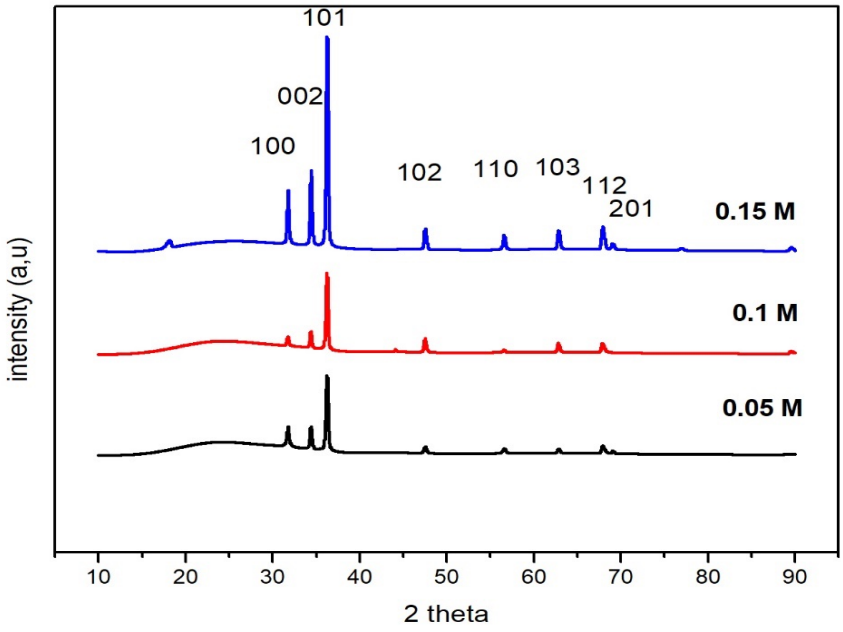

Figure 2. XRD patterns of the ZnO nanorods

polarization and ionic conduction [4]. The electric dipoles in the water molecules align themselves according to the alternating external electric field of the microwaves. The conversion efficiency of electromagnetic wave radiation into heat depends mainly on the dielectric constant of the solution [4]. Microwave radiation can increase the temperature of the solution homogeneously and quickly, which makes it an efficient method for rapid reaction processes.

3.2. Microstructural properties

The X-ray diffraction patterns of ZnO nanorods prepared at three different growth-solution concentrations are shown in figure 2. Based on the reference pattern (ICDD 98-005-7478), the peaks at 2θ 31.72°, 34.36°, 36.20°, 47.48°, 56.54°, 62.78°, 67.88°, and 69.03° correspond, respectively, to the (100), (002), (101), (102), (110), (103), (112), and (201) crystal planes of ZnO. These results show that the material is pure polycrystalline ZnO (without any other phases) and exhibits a hexagonal wurtzite crystal structure. The preferred orientation was quantitatively determined by calculating the value of the Texture Coefficient (TC) [10,11], which showed that the (002) plane had the highest value in all the samples, namely, 1.38, 1.43, and 2.07, for the samples prepared at 0.05, 0.1, and 0.15 M growth-solution concentrations, respectively. These results agree with the morphology images, which show that the nanorods generally grow perpendicular to the substrate (c-axis). Furthermore, it appears that the TC value of (002) increases with increasing growth-solution concentration. This is also in accordance with the morphological observation results in which the nanorod grows more homogenously perpendicular to the substrate. The lattice parameters, cell-unit volumes, interplanar spacing, and crystallite size of the ZnO nanorods in the (002) plane were calculated using the *Highscore* software, as summarized in table 1.

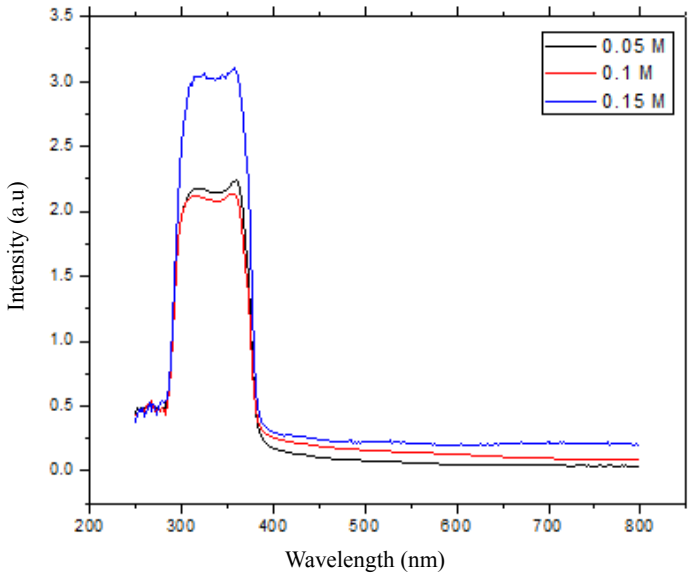

Figure 3. Absorbance spectra of the obtained ZnO nanorods.

Table 1 shows that the lattice parameters and cell-unit volumes of all the samples have values smaller than the standard values under bulk conditions. This may be due to the presence of crystal defects, in the form of oxygen and/or zinc vacancies, which reduce the average value of the lattice parameters and the unit-cell volume. Additionally, increasing the growth-solution concentration slightly increases the value of the lattice parameters a = b from 3.249 to 3.251 Å, as well as the c value from 5.206 to 5.208 Å. In addition, the crystallite size significantly increases from 26.8 to 33.8 and 42.6 nm, which indicates an increase in the crystallinity of the ZnO nanorods formed [12].

3.3. Optical properties

Figure 3 shows the optical absorbance spectra for ZnO nanorods prepared at three different growth-solution concentrations. It is clearly seen that the ZnO nanorods exhibit a high absorption in the wavelength region of 290–375 nm. This has to do with the band gap of ZnO, so the material absorbs photons in the ultraviolet region and these are then used to excite electrons from the valence band to the conduction band. ZnO nanorods prepared at 0.15 M concentration exhibit a higher absorbance than the samples prepared at 0.05 and 0.1 M. This may be associated with the diameter of the nanorods (from SEM results), where the bigger nanorods could be more effective for light absorption.

Figure 3 also shows a sharp curve decline at a wavelength of 375 nm, known as the absorption edge. As the concentration of the growth solution increases, this absorption edge shifts to higher wavelengths. The slope of this curve can be used to determine the band gap of the semiconductor using the Tauc equation, as follows [13]:

$$(\alpha h\nu)^2 = A(h\nu - Eg) \quad (1)$$

where h, ν, and E_g are the Planck constant, frequency, and band gap energy, respectively, and α is the absorption coefficient, which is proportional to the absorbance intensity. To obtain the band gap, $(\alpha h\nu)^2$ is plotted against $h\nu$. The band gap value is then determined by extrapolating the linear curve when $(\alpha h\nu)^2 = 0$, or from the intersection point on the horizontal axis. The band gaps of ZnO nanorods prepared at 0.05, 0.1, and 0.15 M were 3.20, 3.21, and 3.22 eV, respectively. These bandgap values are lower than the ZnO bulk value of 3.37 eV, which is probably due to the presence of crystal defects, such as oxygen and zinc vacancies, that form a new energy level, narrowing the band gap [8]. In addition, it is seen that increasing the growth-solution concentration could slightly increase the band gap.

4. Conclusions

Herein, ZnO nanorods were synthesized on glass substrates by the microwaved-assisted hydrothermal method using varying growth-solution concentrations. Based on our characterization results, we can conclude that increasing the concentration of the growth solution results in increases in the diameter of the obtained ZnO nanorods, the lattice parameters, the volume of the unit cell, and the crystallite size (from 26.8 to 42.6 nm). These changes also lead to an increase in the absorbance intensity in the ultraviolet region as well as to a slight increase in the band gap (from 3.20 to 3.22 eV), which may due to a decrease in the number of oxygen and zinc vacancies.

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