Photoluminescence of ZnO nanorods prepared by hydrothermal method

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Abstract. In this research, the effects of calcination temperature and reaction time on the photoluminescent properties of ZnO nanorods prepared by hydrothermal processes were studied. Morphology, crystalline structure and photoluminescent properties of the prepared samples were analyzed by scanning electron microscope (SEM), X-ray diffractrometer (XRD) and fluorescent spectrophotometer. The study found that a reaction time of 5 hours on a glass slide and calcination at 500°C was the best preparation condition. The prepared ZnO nanorods were aligned without direction and distributed throughout the substrate. The average diameter of the prepared ZnO nanorods was 91.96 ± 21.16 nm. The prepared ZnO nanorods comprised a hexagonal crystalline structure with an emission peak in the UV range.

1. Introduction
The preparation of zinc oxide (ZnO) nanostructures is a popular topic among certain researchers. ZnO is a direct band gap semiconductor with a wurtzite crystal structure. In application, it is used as a filler, varistor, catalyst, photovoltaic, chemical sensor, transparent conductor, etc. In addition, it has been found to exhibit ferroelectric and piezoelectric properties [1-2]. The preparation of the ZnO nanostructures can be done in a variety of ways, such as chemical precipitation [3], spray pyrolysis [4], sol–gel [5], and thermal decomposition [6], as well as electrochemical and hydrothermal methods [7-8]. The hydrothermal method is particularly interesting due to its low cost, low temperature, large scale product, simple process setup and environmental friendliness [8-9]. Various shapes of ZnO nanostructures have been synthesized using the hydrothermal method, including nanobelts, nanowires, nanoflowers and nanoparticles. The effect of the variables on the shape of the ZnO nanostructures was studied, such as hydrothermal time, temperature, precursor concentration, and seed particle size. The different shapes of ZnO nanostructures play a very important role in determining the physical properties of the material.

In this work, we prepared ZnO nanostructures by hydrothermal method and studied the effect of hydrothermal time on the shape, crystal structure and photoluminescent properties of the prepared samples.

2. Experiment
The preparation of ZnO nanostructures in this work is divided into 2 steps: (1) preparation of the ZnO seed layer; (2) preparation of the ZnO nanostructures by hydrothermal method.
2.1. Preparation of the ZnO seed layer
ZnO seed layers were prepared using zinc acetate dehydrate (Zn(CH₃COOH)₂·2H₂O, Univar, 0.1 M) as a precursor dissolved in ethanol and D.I. water, followed by stirring continuously at room temperature for 2 hours. The cleaned glass substrates were then dip-coated 5 times with prepared sol and dried at room temperature.

2.2. Preparation of the ZnO nanostructure
0.02 M zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O, Sigma-Aldrich) and 0.2 M hexamethylenetetramine (C₆H₁₂N₄, Sigma-Aldrich) were dissolved in 100 ml deionized water at room temperature. The ZnO seeds coated glass and ITO substrates were immersed in the aqueous solution. The growth temperature was maintained at 90 °C for 2, 3, 4 and 5 h, respectively. After deposition, the samples were cleaned several times with D.I. water and then dried in air. The prepared samples were calcined at 400, 500, and 600 °C for 1 h in a furnace.

2.3. Characterization
The surface morphology of the prepared ZnO nanorods was collected by scanning electron microscope (SEM: JEOL, JSM-5410LV), while the crystal structure was analyzed by X-ray diffractometer (XRD: PANalytical, X'Pert Pro). Photoluminescence was studied by fluorescent spectrophotometer (HITACHI, F-4600) with an excitation wavelength of 325 nm.

3. Results and discussion
The growth of ZnO nanorods in the hydrothermal process is based on the following chemical reactions [10]:

\[
\begin{align*}
\text{Zn(NO}_3\text{)}_2 & \leftrightarrow \text{Zn}^{2+} + 2\text{N}_3^- \\
\text{C}_6\text{H}_{12}\text{N}_4 + 6\text{H}_2\text{O} & \leftrightarrow 6\text{CH}_2\text{O} + 4\text{NH}_3 \\
\text{NH}_3 + \text{H}_2\text{O} & \leftrightarrow \text{NH}^{4+} + \text{OH}^- \\
\text{Zn}^{2+} + 4\text{NH}_3 & \leftrightarrow [\text{Zn(NH}_3\text{)}]^{2+} \\
\text{Zn}^{2+} + 2\text{OH}^- & \leftrightarrow \text{Zn(OH)}_2 \\
\text{Zn(OH)}_2 & \leftrightarrow \text{ZnO} + \text{H}_2\text{O}
\end{align*}
\]

From equations (1) - (6), it can be seen that the growth of ZnO nanorods depends on the reaction rate and the concentration of Zn²⁺.

Hydrothermal time is an important parameter in the control of the shape and size of ZnO nanorods. Figure 1 shows an SEM image of the ZnO nanorods grown for 2, 3, 4, 5 h. It can be seen that hydrothermal time affects the growth of ZnO nanorods. When the hydrothermal time increases, the diameter of the ZnO nanorods decreases, while length increases. The aspect ratio of the ZnO nanorods at hydrothermal times of 2, 3, 4 and 5 h were 2.15±0.23, 4.33±0.59, 6.48±1.77 and 7.62±1.21, respectively. The XRD patterns of ZnO nanorods prepared at various hydrothermal times are shown in figure 2. The strong peak observed at 2θ of 32.4°, 34.9°, 36.9° and 57.3° correspond to the lattice planes of (100), (002), (101) and (110), respectively. All of these diffraction peaks are assigned to a ZnO hexagonal wurtzite structure (JCPDS no. 361451). The growth process of ZnO nanorods occurs throughout the hydrothermal process and ZnO rods grown along the c axis ((100) direction). The increase in the length of the ZnO nanorods is caused by an increase in the amount of Zn²⁺.
Figure 1. SEM images of ZnO nanorods grown with hydrothermal time of (a) 2 h, (b) 3 h, (c) 4 h and (d) 5 h.

Figure 2. XRD patterns of (a) JCPDS no. 36451 and ZnO nanorods grown with hydrothermal times of (b) 2 h, (c) 3 h, (d) 4 h and (e) 5 h.

Figure 3 shows the PL emission spectra of ZnO nanorods grown with hydrothermal times of 2 h, 3 h, 4 h and 5 h under an excitation wavelength of 325 nm. All ZnO nanorods show two emission bands: 1) a strong emission band (with a maximum around 390 nm) and 2) a weak emission band (with a maximum around 470 nm). The first band in the UV region is attributed to the recombination of free excitons through exciton-exciton collision. The second band is created by the presence of structural defects and impurities [11-12].
Figure 3. PL emission spectra of ZnO nanorods grown with hydrothermal times of 2 h, 3 h, 4 h and 5 h.

Figure 4 shows the effect of calcination temperature on the crystal structure of ZnO nanorods. It can be seen that a peak at position 20 of 32.4°, 34.9°, 36.9° and 57.3° is still found at calcination temperatures of 400 °C and 500 °C. At a calcination temperature of 600 °C, only a peak at 32.4° is found. In addition, it is found that the intensity of the peak decreases when the calcination temperature increases, indicating less crystallinity, which affects the intensity and position of the emission, as shown in figure 5.

Figure 4. XRD patterns of (a) JCPDS no. 36451 and ZnO nanorods at calcination temperatures of (b) 400 °C, (c) 500 °C and (d) 600 °C.
Figure 5. PL emission spectra of ZnO nanorods at calcination temperatures of 400 °C, 500 °C and 600 °C.

4. Conclusion
We synthesized ZnO nanorods by hydrothermal method. From the study, it was found that hydrothermal time directly affects the aspect ratio and emission spectra of ZnO nanorods. The synthesized ZnO nanorods in this study showed a strong UV-PL at 392 nm, owing to the recombination of free excitons through an exciton-exciton collision. When the calcination temperature is too high, it results in PL emission due to the surface being damaged. Therefore, our research shows the effect of hydrothermal time and calcination temperature on the PL emission of ZnO nanorods. The results of this research could serve as a guideline for improving the method used for synthesizing ZnO nanorods with intense emission. ZnO nanorods with intense emission may have potential application in optoelectronic devices.

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References
[1] Bøjesen E D, Jensen K M Ø, Tyrsted C, Lock N, Christensen M and Iversen B B 2014 *Cryst. Growth. Des.* **14** 2803
[2] Peng W, Qu S, Cong G and Wang Z 2006 *Cryst. Growth. Des.* **6(6)** 1518
[3] Kumar P S and Nesaraj A S 2017 *Int. J. Pharm. Bio.* **8(1)** B232
[4] Krunks K, Bijakina O, Mikli V, Varema T and Melikov E 1999 *Phys. Scr.* **T79** 209
[5] Hasnidawani J N, Azlina H N, Norita H, Bonnia N N, Ratim S and Ali E S 2016 *Procedia Chem.* **19** 211
[6] Khalil M I, Al-Qunaibit M M, Al-zahem A M and Labis J P 2014 *Arab. J. Chem.* **7** 1178
[7] Mah C F, Yam F K and Hassan Z 2016 *Procedia Chem.* **19** 83
[8] Tam K H et al 2006 *J. Phys. Chem. B* **110** 20865
[9] Alshehri N A, Lewis A R, Pleydell-Pearce C and Maffeis T G G 2018 *J. Saudi. Chem. Soc.* **22** 538
[10] Kamruzzaman M and Zapien J A 2018 *Crystallogr. Rep.* **63(3)** 456
[11] Musa I, Qamhieh N and Mahmoud S T 2017 *Results Phys.* **7** 3552
[12] Yim K G et al 2012 *Acta. Phys. Pol. A* **122** 214