# SYNTHESIS AND PHOTOLUMINESCENCE PROPERTIES OF ZnO WITH WET-CHEMISTRY TECHNIQUES

L. M. DONG[a,b*], K. J. WU[a], X. J. LI[a], Z. D. HAN[a,b]
[a]*College of Materials Science and Engineering, Harbin University of Science and Technology, Harbin, China*
[b]*Key Laboratory of Engineering Dielectrics and Its Application, Ministry of Education, Harbin University of Science and Technology, Harbin, China*

ZnO nanostructures were synthesized by two wet chemical methods including hydrothermal method and sol-gel method. Morphology, structure and photoluminescence properties of the prepared samples were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and fluorescence spectrophotometer. The ZnO nanorods prepared by the hydrothermal method had a diameter under 100 nm and grew along with the [0001] direction, meanwhile the ZnO nanospheres synthesized by the sol-gel method also possessed a diameter under 100 nm. The growth mechanisms of ZnO with different morphologies were discussed. We found that the morphologies of ZnO were related to the concentration of $OH^-$. Photoluminescence (PL) measurements confirmed that the ZnO nanostructures exhibited a blue emission with a luminescent center of 466 nm.

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*Keywords*: ZnO nanostructures, Hydrothermal, Sol-gel, Photoluminescence properties

## 1. Introduction

As a multi-function wide band gap semiconductor material, wurtzite ZnO – with a direct band gap of 3.37 eV, a large exciton binding energy of 60 meV at room temperature (RT) which is larger than those widely used semiconductors GaN (26 meV) or ZnSe (20 meV) and also larger than the RT thermal energy (25 meV) – has attracted the attention of researchers for several decades due to its important applications, especially in optics and optoelectronics[1-6]. ZnO not only owns excellent optical and electrical properties, but also has many nanostructures with different morphologies, such as spheres, rods/fibers/wires, thin films, and multipods. It is significant to study and explore the unique properties of ZnO. Various chemical, electrochemical, and physical deposition techniques have been reported in preparing ZnO nanostructure. For instance, ZnO nanocrystals in high quality are mainly fabricated in metal-organic chemical vapor deposition (MOCVD)[7-10] or pulsed laser deposition[11] method. But those technologies require high expenses on equipments, which limits the practical applications of ZnO nanomaterials. On the other hand, the wet-chemistry techniques are now promising options for preparing large scale ZnO nanomaterials at low cost and under remarkably low temperature conditions[12-15]. The morphology and characteristics of the wet chemistry-derived ZnO crystallites can be varied by changing the origin materials, the reactant concentrations, procedural details, and reaction temperature and time.

In this preliminary work, we used a composed of zinc nitrate ($Zn(NO_3)_2$) and citric acid in the sol-gel technique, and synthesized the nanospheres of ZnO. Zinc nitrate ($Zn(NO_3)_2$) and

*Corresponding author: donglimin@hrbust.edu.cn

ammonia water ($NH_3•H_2O$) were used in the hydrothermal technique and the nanorods of ZnO were achieved. The details of the preparation process will be shown in this paper. Moreover, the impact of $OH^-$ concentration on the properties of the final production was investigated and the possible formation mechanisms have been discussed.

## 2. Experimental

### 2.1 Preparation of ZnO nanorods

ZnO nanorods were prepared by the hydrothermal method with orthogonal experiment (four factors and five levels). Analytical-grade of zinc nitrate ($Zn(NO_3)_2$, AR) and ammonia water ($NH_3•H_2O$, AR) were selected as original materials. $Zn(NO_3)_2$ was the source of $Zn^{2+}$, and $NH_3•H_2O$ acted as the supplier of $OH^-$. $Zn(NO_3)_2$ was dissolved into water, then the pH of the solution was adjusted to 8-12 with $NH_3•H_2O$. Following the mixture solution was transferred to a 150 mL Teflon-lined stainless steel autoclave and the hydro-thermal reaction proceeded at 160-200℃ for several hours. After the reaction, the product was washed with deionized water and absolute ethyl alcohol for several times. Then the precipitate was put into the vacuum drying oven at 100℃ for 24 h, finally the ZnO nanorods were achieved.

### 2.2 Preparation of ZnO nanospheres

ZnO nanospheres were prepared by the sol-gel method. Analytical-grade of zinc nitrate ($Zn(NO_3)_2$) and citric acid were selected as original materials. Citric acid acted as both stabilizer and mineralizer. 0.5837 g citric acid ($C_6H_8O_7•H_2O$, AR) and 0.826 g zinc nitrate ($Zn(NO_3)_2$, AR) were dissolved into water. After stirring for 30 min, the mixture solution aged in the next 12 h at room temperature. Then the mixture solution was evaporated and concentrated until changing to wet-gel at 80℃ oil-bath. Then the wet-gel was put into vacuum drying oven at 100℃ for 8 h, and the xerogel formed. The xerogel was calcined at 500℃ for 2 h, and the ZnO nanospheres was achieved.

### 2.3 Characterization

The resulting phase formation was identified by X-ray diffraction (XRD, Rigaku D/MAX-RB, Japan) with Cu-Kα radiation (λ=0.154056 nm). Morphological features of the samples were observed using field emission scanning electron microscopy (FE-SEM, Sirion200, Philip) and transmission electron microscopy (TEM, JEM2100, Japan). Photoluminescence (PL, RF-5301PC, Shimadzu, Japan) spectra were measured at room temperature using a HeGd laser with a wavelength of 335 nm as the excitation source.

## 3. Result and Discussion

### 3.1 XRD analysis

The crystal structures of the synthesized samples were determined by powder X-ray diffraction (XRD) using a copper Kα radiation source at 40 kV and 200 mA in steps of 0.02. Data were recorded ranging from 10° to 90°. Fig. 1 showed the XRD patterns of as-synthesized samples obtained by hydrothermal method which was reacted at 180℃ for 10 hours and adjusted pH to 11, while the sol-gel method was prepared as the work in the part 2.2, whose reflection peaks both can be readily indexed with the wurtzite ZnO (JCPDS No. 79-2205). When the ZnO nanospheres was obtained by the sol-gel method, it was namely the sample B. When the ZnO nanorods was prepared by hydrothermal method, it was namely the sample A. We noted that the intensity of the peaks of sample A was stronger than the sample B. Some crystal intensity of sample A was much stronger than the sample B. We imagined that the crystal structures of sample A were different of sample B.

The crystal structure of ZnO was shown in Fig.2, which belonged to the wurtzite structure. It can be seen that lattice parameters were a=0.3249 nm and c=0.5206 nm.

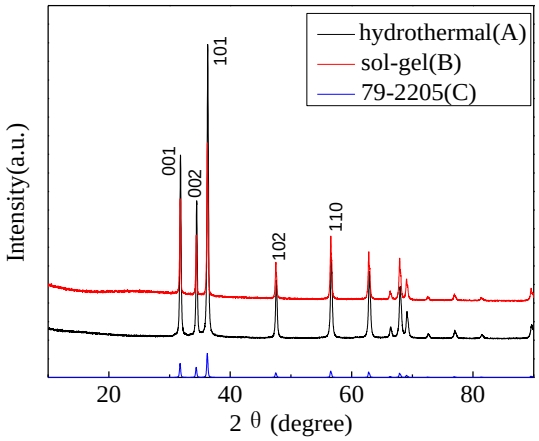


*Fig. 1. XRD spectra of ZnO synthesized by:*
*(a) sol-gel (b) hydrothermal (c) JCPDS No. 79-220.*

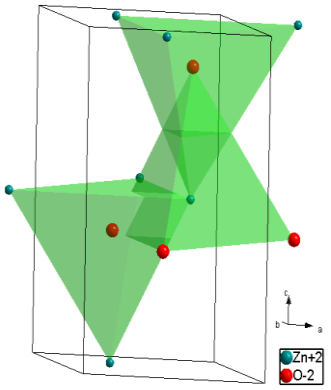


*Fig. 2. Crystal structure of ZnO*

**3.2 Morphology analysis**

SEM images of the products were shown in Fig. 3. Sample A was prepared by hydrothermal method calcined at 200℃ for 10 hours and pH was 8. Sample B was prepared by the sol-gel method in this paper. It is apparent that ZnO prepared by hydrothermal method and sol-gel method both look like nanospheres, but from transmission electron microscope (TEM) at top right corner we can see that the morphology of ZnO prepared by hydrothermal method is actually nanorods. We supposed that the morphologies of ZnO were connected with the concentration of $OH^-$. In order to prove this conjecture, we made the following experiment as Fig. 4.

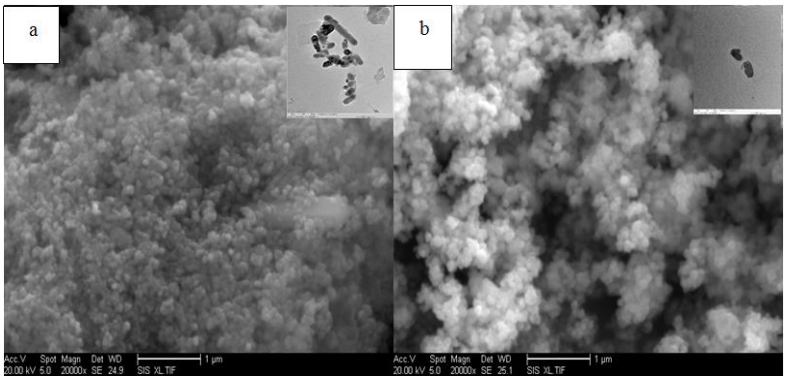


*Fig. 3. SEM images of ZnO: (a) hydrothermal method (b) sol-gel method*

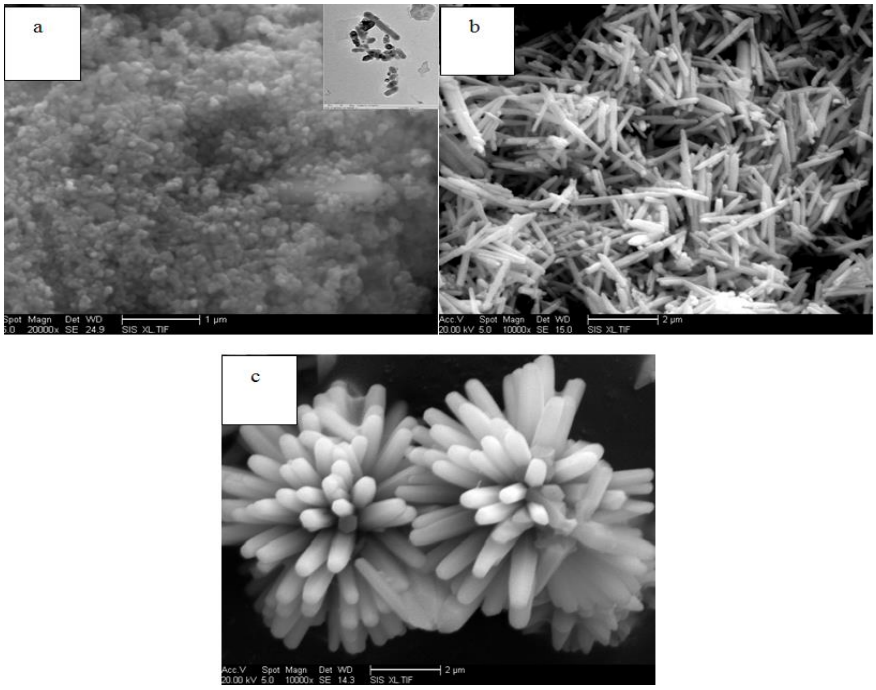


*Fig. 4. SEM images of ZnO by hydrothermal method at different pH: (a)pH=8 (b)pH=10 (c)pH=12*

Fig. 4 was ZnO SEM images at different alkaline conditions. When pH was 8, ZnO looked like nanospheres, and diameter was under 50 nm, as shown in Fig. 4(a). When pH was 10, a large number of nanorods appear, and diameter was about 100-200 nm, as shown in Fig. 4(b). When pH was 12, nanorods form the shape of flowers, diameter was about 500 nm, as shown in Fig. 4(c).

Zinc oxide growth process included the formation of growth units ($Zn(OH)_4^{2-}$) and the dehydration of growth units at crystal growth interface. $Zn(OH)_4^{2-}$ was a tetrahedral structure, and Zinc element was located in the middle and $OH^-$ was in the four vertices. In the process of ZnO crystal growth, $OH^-$ was the connection of the two vertices of the tetrahedron taking off the water to complete the growth process and the growth direction along the c-axis of ZnO. The growth rate of the crystal face and coordination polyhedra ($ZnO_4$) with the number of $OH^-$ that on each side of the interface family showed positive relationship. Under the condition of low concentration of $OH^-$ (pH=8), the difference of the number of $OH^-$ dangling bonds family units on each side was smaller, and $OH^-$ had little influence on the crystal growth rate. And the formation of ZnO crystal nucleus was slower, so that there was enough time to gather and grow together. Therefore, the ZnO structure that looks like spherical particles can be obtained, as Fig. 4(a) and Fig. 3(b) showed. When the concentration of $OH^-$ was high (pH=10), $Zn^{2+}$ was surrounded by more $OH^-$ and then each side of the interface showed the number of $OH^-$ with obvious difference, so that the growth speed of the face had a bigger difference. By the growth habit laws of ZnO coordination polyhedron, the fastest growth direction was [0001]. This result was consistent with the experimental results. When the concentration of $OH^-$ was higher (pH=12), petal-shaped cylindrical hexagonal ZnO could be got.

### 3.3 Performance analysis

Fig.5 showed the emission spectra of the ZnO prepared by hydrothermal method and sol-gel method.

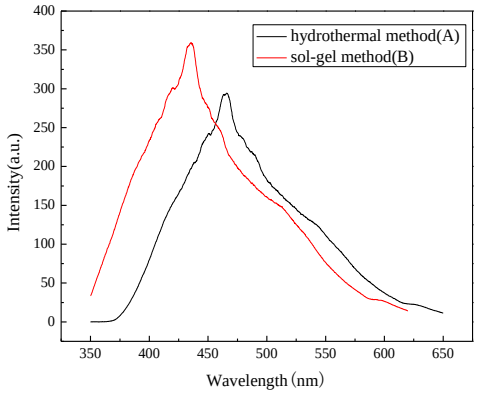


*Fig.5. PL spectra of the ZnO*

As we can see from Fig.5, the ZnO nanostructures prepared by sol-gel method (sample B) exhibited a higher purple-blue emission and the emission peak centered at 435 nm, while the ZnO nanostructures prepared by hydrothermal method (sample A) exhibited a blue emission that was centered at 466 nm. We can know that fluorescence intensity of sample B was stronger than sample A, while a blue shift occurred at sample A. We recognized that the crystal surface [0001] leading to this phenomenon.

## 4. Conclusion

A novel blue phosphor ZnO was prepared by hydrothermal method and sol-gel method. And the structure, morphology and fluorescence properties of the ZnO nanostructures were studied. It was found that the morphologies of ZnO were connected with the concentration of $OH^-$ and the ZnO nanostructures exhibited a blue emission.

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