



# SYNTHESIS OF ZnO NANOSTRUCTURES BY HYDROTHERMAL METHOD

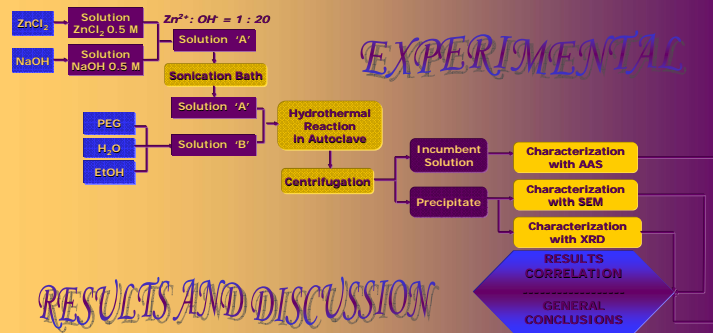
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## INTRODUCTION

- Zinc oxide (ZnO) is an important multifunctional semiconductor with a wide bandgap (3.4 eV). It has a stable wurtzite structure with lattice spacing of  $a=0.325$  nm and  $c=0.521$  nm [1-4]. It has attracted much research interest due to its unique optical, acoustic, luminescent, electronic and optoelectronic properties
- Many methods have been used to prepare the ZnO material as one-dimensional (1D) nanostructures with different morphologies including nanowires, nanorods, nanotubes, whiskers, nanocrystals, nanobelts and other superstructures [1,3,5]. They represent a broad class of nanoscale building blocks that have been used to assemble functional devices such as lasers, photodetectors, field emitters, acoustic and short wavelength optical devices, gas sensors, piezoelectric transducers and actuators, solar cells etc [3,5-7]
- There are several methods to synthesize ZnO nanostructures, such as vapour transport process catalyst free (vapour-solid process / VS) or catalyst assisted (vapour-liquid solid process / VLS), epitaxial electrodeposition (ED), sol-gel method, polymer assisted growth, metal-organic chemical vapour deposition (MOCVD), pulsed laser deposition (PLD), aqueous chemical methods and hydrothermal methods [1,7]
- Low temperature hydrothermal synthesis (at 95 °C or between 150 – 250 °C) is becoming popular for environmental reasons, since water is used as the reaction solvent than organics. This method is also more convenient and economic for large-scale preparation of well-ordered ZnO nanowire/nanorod arrays compared to VLS, CVD and ED methods, which require sophisticated equipment and rigorous conditions (such as single-crystalline substrates) [10]

The aim of this work is firstly to synthesize ZnO nanostructures by hydrothermal method and secondly to investigate the influence of water, ethanol (EtOH) and polyethyleneglycole (PEG) and the reaction time at constant temperature on the morphology / dimensions and structure of the final products



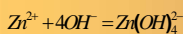
## RESULTS AND DISCUSSION

The raw materials and conditions for the hydrothermal synthesis of ZnO nanostructures are presented in Table 1.

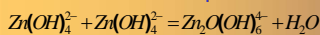
Table 1. Raw materials and conditions for the hydrothermal synthesis of ZnO nanostructures

MATERIALS	Solution 'A'		Solution 'B'			Hydrothermal Treatment at 200 °C	
	10 M NaOH & 0.5 M ZnCl <sub>2</sub> (molar ratio of Zn <sup>2+</sup> :OH <sup>-</sup> = 1:20)		H <sub>2</sub> O (mL)	Ethanol (mL)	Polyethylene glycol (PEG) (g)	Pressure (bar)	Incubation Time (h)
1Z-1	10	20	50	0.02	10	1	
1Z-3	10	20	50	0.02	10	3	
5Z-1	10	20	50	1.60	11	1	
4Z-1	10	-	70	0.16	21.5	1	
2Z-1	15	105	-	0.03	7	1	
2Z-3	15	105	-	0.03	7	3	
2Z-20	15	105	-	0.03	7	20	
9Z-1	15	105	-	0.03	7	1	

According to literature [5] the growth unit of ZnO crystal is the complex  $Zn(OH)_4^{2-}$ . The formation mechanism of ZnO crystallite under hydrothermal condition begins with the formation of the growth unit:



and proceeds with the incorporation of growth unit into the newly formed crystal lattice by the oxolation reaction under supersaturation condition:



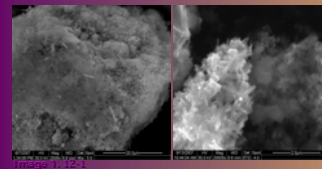
Finally, when the size of the clusters  $Zn_{2n+1}O_{n+1}OH_{c+2n-2c+2}^{(c+2)-}$  reaches the size of the so-called "critical nucleus", ZnO powders are precipitated

For the quantification of the unreacted Zn contained in the incubant solution as received from the autoclave after the completion of the reaction, the procedure is as follows: the incubant solution is volumetric measured and 1 mL of this solution is diluted with bidistilled water to form a diluted solution of 250 mL, and then the percentage of unreacted Zn is measured with Atomic Absorption Spectroscopy (AAS). The results are presented in Table 2, whereas the amount of Zn in the incubant solution is calculated in percentage and the difference corresponds to the percentage of reacted Zn. The yield of Zn is high fluctuating approximately between 90 and 96 % w/w.

Table 2. Amount of Zn containing in the incubant solution determined by AAS and amount of reacted Zn

Incubant solution of experiments	Volume of the incubant solution (mL)	Measured Zn in the incubant solution by AAS (ppm=mg/L)	Percentage of reacted Zn (%)
2Z-1	106	0.397	95.71
4Z-1	49,5	0.758	94.26
9Z-1	110	0.885	90,01

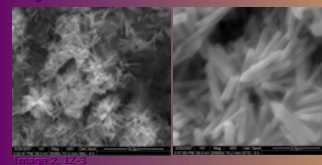
Based on the SEM images (Images 1-8), the final products show a growing behaviour along the c-axis with morphologies of straight or flowerlike / starlike rods, either ending with regular hexagonal prism or with hexagonal pyramid



Material 1Z-1 (Image 1) consists of mainly amorphous material and very few single rods or rods in branched structures deposited on it

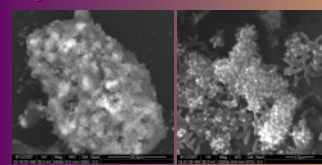
The material received after 3 h (Image 2 / 1Z-3) consists of a) single rods, b) few flowerlike or starlike branched structures and c) amorphous material covered with a and b

Most rods of this material, either alone or branched have ends with regular hexagonal pyramid structure



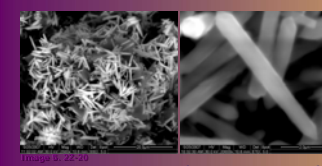
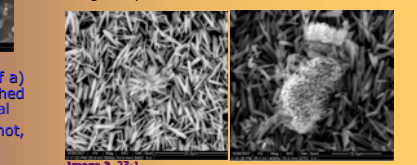
In the material 5Z-1 (Image 7) there are a) single rods, b) many flowerlike or starlike branched structures, c) some amorphous material covered with a) and b) forms

It is characteristic for this material that the rods, branched or not, have ends with regular hexagonal prism structure



The material 4Z-1 (Image 6) consists of a) very few single rods, b) very few branched rods and c) much of amorphous material

All rods of this material, branched or not, have sharp ends



In Image 3, material 2Z-1 consists of a) single rods, b) few flowerlike or starlike branched structures and c) a tuft made of oriented whiskers

The same material received after 3 h (Image 4 / 2Z-3) or 20 h (Image 5 / 2Z-20) give similar products of a) single rods and b) flowerlike or starlike branched structures

The material 9Z-1 (Image 8) consists of a) single rods, b) flowerlike or starlike branched structures and c) some amorphous material covered with a) and b) forms. The rods, branched or not have ends with regular hexagonal pyramid structure.

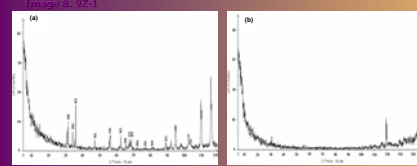


Figure 1. X ray diffraction patterns of materials (a) 2Z-1 and (b) 4Z-1

The above observation is also confirmed by SEM images concluding that material 4Z-1 has much of amorphous regions. The diffractograms of materials 2Z-1, 2Z-3, 2Z-20 and 9Z-1 exhibit high crystallinity.

The material which is in the form of flowerlike or starlike structures (5Z-1) has a variety of orientation and a low crystallinity is observed from its diffractogram

## CONCLUSIONS

By increasing the incubation time, the amorphous regions are decreased and more rods, branched or not with ends of regular hexagonal pyramid structure are formed and their dimensions are increased (comparison between 1Z-1 and 1Z-3)

By increasing the proportion of PEG, the amorphous regions are further reduced and many flowerlike or starlike branched structures are formed, which have ends with regular hexagonal prism structure (comparison between 1Z-1 and 5Z-1)

The use of ethanol without water (4Z-1) leads to very few single or branched rods and much of amorphous material, therefore water is necessary to be used in the initial solution for the hydrothermal process (comparison between 1Z-1 and 4Z-1)

On the other hand, the use of increased amount of water, without ethanol (materials 2Z-1, 2Z-3, 2Z-20, 9Z-1) leads to the formation of nanostructured material without amorphous regions, in the forms of single rods or branched, forming flowerlike or starlike structures with ends of regular hexagonal pyramid structure. Under these conditions, ZnO nanostructures are sufficiently formed already by one hour, and extended time does not contribute to any improvement in the nanostructures

Comparing the ZnO structures of this group of materials (second group, materials 2Z-1, 2Z-3, 2Z-20, 9Z-1) with that of the first group (1Z-1, 1Z-3, 5Z-1, 4Z-1), it is observed that the particle dimensions are greater for the second group

Although the precipitation yield is very high, not all products are in crystalline nanostructure form, as is observed in SEM images and in X ray diffraction patterns

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