

## Pulsed Microwave Aided Morphology Controlled Synthesis of Nano Zinc Oxide

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**Abstract:** Here we present a morphology controlled growth of nano ZnO through variation in precursor composition and controlled microwave (MW) exposure time. The ZnO nanostructures are synthesized by MW aided co-precipitation method. The SEM micrograph shows that the as obtained ZnO nanostructures show significant variation in morphologies like flowers, tubes and sheets with variation in precursor and MW exposure time. An analytical model is presented to explain the growth mechanism of various morphologies. The crystal growth habit shows a remarkable change with morphology. The as obtained ZnO nanostructures emit in the blue and green visible region.

**Keywords:** Controlled Synthesis, Microwave aided method, Optical properties, nanostructure, ZnO.

### I. Introduction

The growth behaviour ZnO nanomaterial is significantly affected by the external conditions such as reaction timing, reaction temperature, reaction concentration, pH value of the solution [1–2]. Concentration of OH<sup>-</sup> ions in the solution affects the hydrolysis process of ZnO formation, and hence it shows influence on morphology of material. We have already reported in our previous work [3], that growth unit (OH<sup>-</sup>) is responsible for growth of complex structures. Mostly nanomaterials are reported to be synthesized with special environment, sophisticated instruments and methods. In this work, we have fabricated nanostructures through MW pulse assisted method. MW assisted methods have been considered as a powerful method for synthesis of highly crystalline, defect free nano particles with controlled size and shape [4]. This method is easy to handle, cost effective and less energy consuming, hence it is a green method. The growth mechanism and morphology depends on various factors like availability of precursors, pH and temperature of the bath, rate of nucleation and growth, solvents used etc [5]. The MW heating imparts very high energy uniformly, thereby generating numerous nucleation sites, responsible for high yield. Further the MW exposure time controls the morphology and size of the NPs [4]. So MW assisted co precipitation method was used for the present study.

### II. Experimental Method

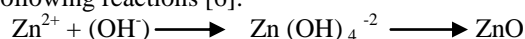
All chemicals were analytical grade (Merck), and were used without further purification. ZnO nanostructures were synthesized through the MW aided hydrolysis of Zinc acetate dihydrate Zn (CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O, using Lithium hydroxide (LiOH) as a base. The samples were prepared with variation in molar ratio of Zn (CH<sub>3</sub>COO)<sub>2</sub>·2 H<sub>2</sub>O to LiOH (Zn<sub>(M)</sub>: LiOH<sub>(M)</sub>: 1:10, 1:20, 1:25) dissolved in 100 ml distilled water and then were kept into domestic MW oven at 300W (on: off ratio being 12s: 10s respectively) and also with variation in the MW irradiation exposure time e.g. 10, 20 and 40 min. The resulted precipitate was collected, washed with ethanol and DD water several times and finally dried in air at 80°C for 24 h.

For structural characterization, X-ray diffraction (XRD) patterns were obtained by using Bruker “D2 PHASER” diffractometer. Photoluminescence (PL) emission spectra were taken with the help of Shimadzu RF 5301 PC Spectrofluoro-photometer and the morphological characterization is carried out by Scanning electron microscope “ZEISS EVO 18”.

### III. Results and Discussion

#### 3.1 Effect of molar ratio variation on morphology

Zinc acetate and LiOH were used as Zn<sup>2+</sup> source and OH<sup>-</sup> source respectively. OH<sup>-</sup> ions help the formation of ZnO 1-D and 2D nano forms in the wet chemical synthesis [6,7]. The growth mechanism can be understood on the basis of the following reactions [6]:



The crystal habits of wurtzite ZnO as presented in the schematic diagram in Fig. 1. The basic growth unit is [Zn(OH)<sub>4</sub>]<sup>2-</sup> in the solution-based method to grow ZnO nano forms by the reaction of Zn<sup>2+</sup> ions with the OH<sup>-</sup> ions [8] further it is changed in ZnO. The crystal habit of wurtzite ZnO exhibits well-defined crystallographic faces such as polar-terminated (0001) and non-polar low-symmetry (1010). One face of the hexagonal sheet is Zn rich and forms the (0001) planes, whereas the opposite face is the (000-1) plane. Thus, the

ZnO crystals are polar in nature, and the Zn-rich positive (0001) surface being more reactive than the oxygen-rich negative (000-1) surface can attract new ZnO species or the opposite ionic species to its surface to promote anisotropic growth along the (0001) direction. It will be interesting to explore the growth mechanism of various morphologies of the as obtained 1D and 2D ZnO NPs. An analytical model is given in Fig.1 to explain the growth mechanism.

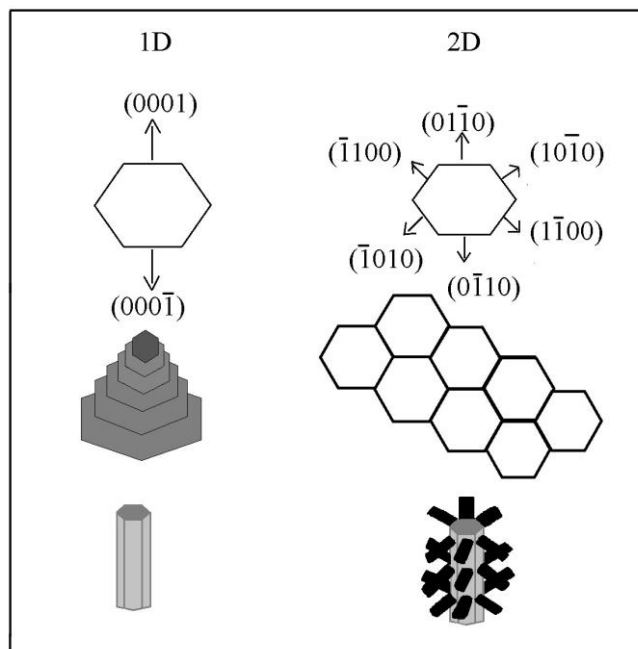


Fig.1 Schematic Representation of Growth Mechanism of 1D and 2D Nanostructures.

The six side facets are generally bound by the (10-10) family of planes as shown in Fig.1. The growth rates of planes of wurtzite ZnO follow the sequence  $(0001) > (10-11) > (10-10)$ . Normally ZnO columnar structures bound by six (10-10) facets are grown along the (0001) direction the presence of a smaller amount of  $\text{OH}^-$  caused the reaction to proceed much more slowly, and hence, the initial nucleus had sufficient time to grow in the lateral directions, resulting in the formation of nanosheets where as the presence of the  $\text{OH}^-$  ions in high concentration induces longitudinal growth along the (0001) direction, and to maintain the lowest possible energy, six low-energy facets appear, preventing the lateral growth. As the amount of the LiOH was increased slowly, the increase in the concentration of the  $\text{OH}^-$  ions increased the production of the growth unit  $[\text{Zn}(\text{OH})_4]^{2-}$ , resulting in the formation of nanorods.

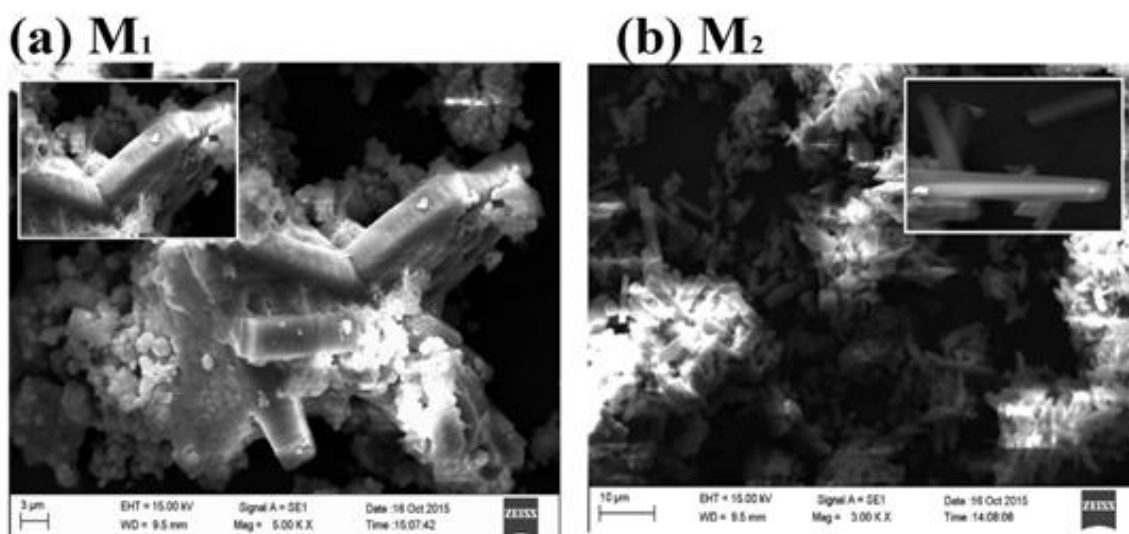


Fig.2 shows the SEM images of ZnO structures grown with various molar ratio of the base LiOH (a)  $M_1$ , (1:10) (b)  $M_2$  (1: 25).

It can be observed that the morphology significantly depends on the molarity of precursor solution. Fig.2 shows morphology of ZnO nanostructures. A 2D ZnO nanosheet structure is formed in sample M<sub>1</sub>, which was prepared with a lower molar ratio of 1:10 of Zn<sup>+2</sup>: OH<sup>-</sup>. Whereas a 1D ZnO nanorod structure was obtained in case of sample M<sub>2</sub>, when the molar ratio of Zn<sup>+2</sup>: OH<sup>-</sup> was increased to 1:25. Addition of Zinc acetate dihydrate and Lithium hydroxide in water in presence of microwave irradiation results in a white precipitate, containing Zn (OH)<sub>2</sub> and growth unit Zn (OH)<sub>4</sub><sup>2-</sup> in aggregated form. The growth units of ZnO arrange themselves in water solvent, in presence of microwave irradiation pulse. In many research reports, ZnO nanostructures have been synthesized in presence of continues microwave irradiation [9, 10] however, in present study microwave irradiation was given in pulsed form, leading to a homogenous nucleation, as has been reported by few other researchers [11]. As the molarity of the base increases, the numbers of OH<sup>-</sup> ions are released in large amount, which led to the growth of nanostructure as nanorod [12], whereas a lower concentration of OH<sup>-</sup> ions led to horizontal growth leading to flat 2D structure [6,13]. So, this is evident in the present study that the number of OH<sup>-</sup> ion on the surface of nanostructure is responsible for growth in (0 0 0 1) plane. Table 1 complies the data of structural study.

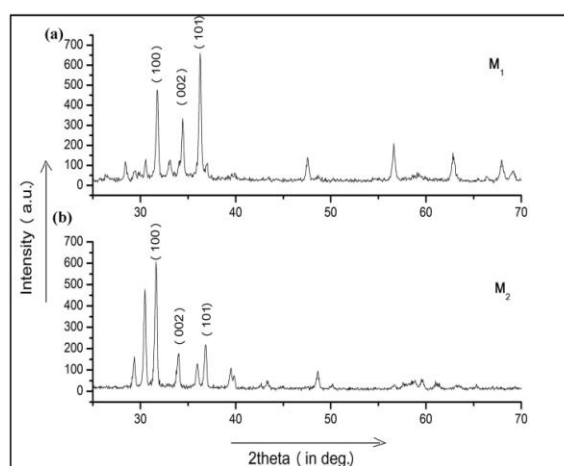
**Table1** Compilation of structural and morphological variation with change in molar ratio of Zn<sup>+2</sup>: OH<sup>-</sup>

Sample Name	Molar ratio Zn <sup>+2</sup> :OH <sup>-</sup>	Reaction Time	Particle Size	Morphology	Peak	2Θ(°) Standard	2Θ(°) Observed	Observed Intensity (a.u.)
M <sub>1</sub>	1:10	20 min	32.82nm	Nanosheet	100	31.77	31.78	438
					002	34.42	34.44	276
					101	36.26	36.27	611
M <sub>2</sub>	1.25	20 min	32.82nm	Nanorod	100	31.77	31.65	567
					002	34.42	33.99	149
					101	36.26	36.84	191

Fig.3 shows the XRD patterns of the as prepared ZnO nanostructures of samples M<sub>1</sub> and M<sub>2</sub>. The Characteristic peaks of ZnO are observed as per the COD file number (9011662, 9008877,1011258) in the XRD pattern. The sharpness of peaks shows good crystallinity of samples. The particle size of these nanostructures is calculated through the Debye-Scherrer formula [14]:

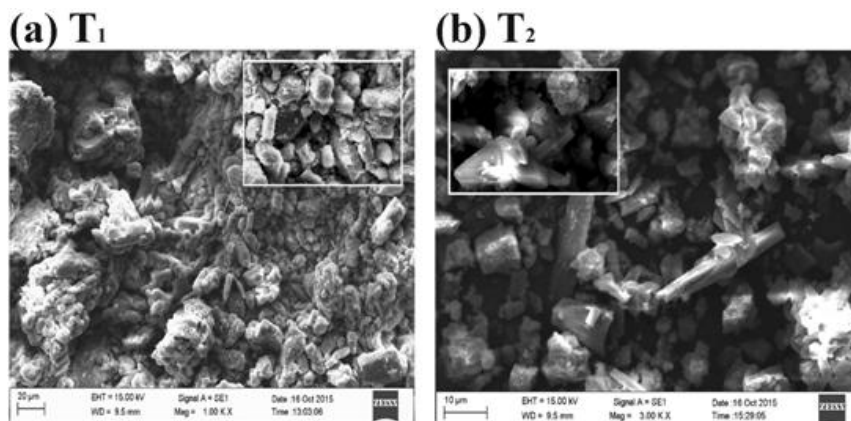
$$D = \frac{0.9\lambda}{\beta \cos \theta}$$

Where, D is particle size, λ is the wavelength of Cu Kα and β is the full width at half maximum and θ is diffraction angle. Presence of (001) (002) and (101) peaks in XRD graph indicates the hexagonal structure of ZnO.



**Fig.3.** XRD graph of ZnO nanostructure prepared with various molar ratio of the base LiOH (a) , (1:10) (b) M<sub>2</sub> (1: 25)

On comparing the XRD patterns of samples M<sub>1</sub> and M<sub>2</sub>, a variation in intensity of peak ( 100) is observed at the cost of intensities of (002) and (101) peaks in case of M<sub>2</sub>, which has 1D structure. These kinds of structural changes peaks have already reported for 1D and 2D structures of ZnO [15,16]. Further, Samples T<sub>1</sub> and T<sub>2</sub> were synthesized with variation in MW exposure time with a fixed molar ratio of Zn<sup>+2</sup>:-OH. Fig.4 shows the SEM micrograph of samples T<sub>1</sub> and T<sub>2</sub>. For shorter exposure the ZnO NPs with irregular shapes can be observed, containing a mixed matrix of nano dots, elongated spheres, and tiny rods.

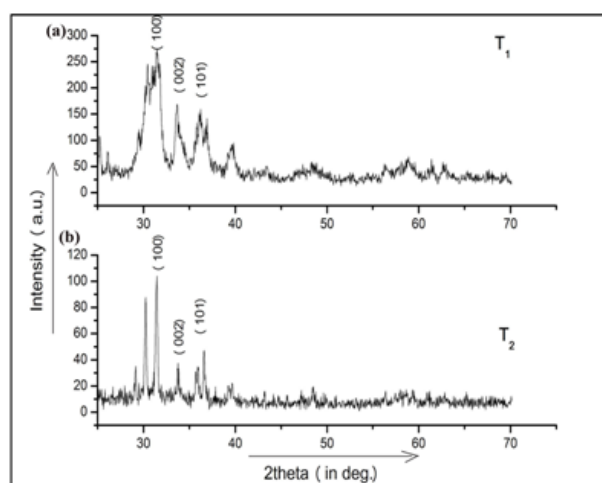


**Fig.4.** SEM graph ZnO nanostructure of temperature variation (a) T<sub>1</sub>, 40 min pulsed MW exposure (b) T<sub>2</sub>, 10 min pulsed MW exposure.

These irregular morphologies show an interesting growth mechanism. We propose that at the beginning of crystal formation, various structures can be formed, out of which only those sustain for which favourable growth conditions persist. It also indicates that a certain reaction time is required, for perfect nucleation or preparation of well shaped nano material. The SEM for sample T<sub>1</sub> with longer exposure time shows uniform crystals with hexagonal ends. So we can conclude that as we increase the exposure time those crystals which have favourable conditions grow at the cost of others, thus leading to dominance of a particular morphology [17, 18]. The XRD studies further confirm this observation. From Fig.5, Broad overlapping peaks (100) are observed in sample T<sub>1</sub> with 40 minutes exposure of MW pulses. This broadening indicates presence of smaller Nanocrystals [19]. Whereas, in case of T<sub>2</sub>, the MW exposure time was just 10 minutes, which led to bigger crystals, resulting in sharp and intense peaks. The process of crystal growth is a dynamic process where the dissolution and creation of crystals takes place continuously and simultaneously. The decrease in particle size with increasing MW exposure time can be due to growth of NPs with a favourable morphology at the cost of bigger crystals with varied morphology [20]. Table 2 shows the effect of MW exposure time on the particle size as reaction time is increased the size of nanomaterial is decreased [21].

**Table 2** Effect of MW exposure time on structure and morphology of ZnO NPs

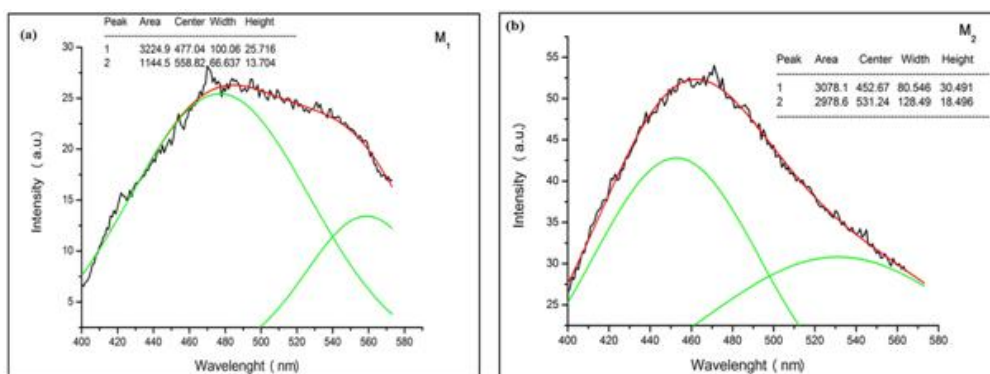
Sample Name	Molar ratio Zn <sup>2+</sup> :OH	Reaction Time	Particle Size) In nm	Morphology	Peak	2θ Standard(in °)	2θ Observed (in °)	Observed Intensity (a.u.)
T <sub>1</sub>	1:20	40 min	20.20	Small tube	100	31.77	31.51	215
					002	34.42	33.62	114
					101	36.26	36.24	104
T <sub>2</sub>	1.20	10 min	32.82	Irregular	100	31.77	31.43	86.9
					002	34.42	33.72	21.6
					101	36.25	36.67	37.8



**Fig.5.** XRD graph ZnO nanostructure of temperature variation (a) T<sub>1</sub>, 40 min pulsed MW exposure.(b) T<sub>2</sub>, 10 min pulsed MW exposure.

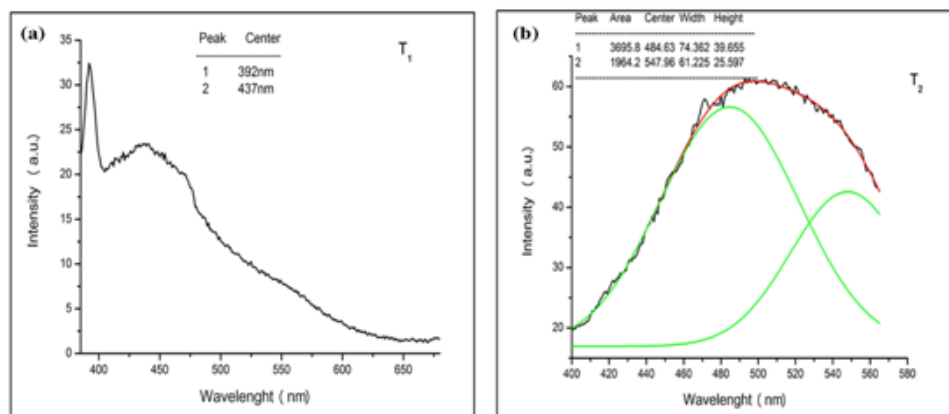
### 3.2 Effect of Molarity and MW exposure time variation on optical properties of ZnO NPs

The optical property of the as synthesized ZnO nanostructure with different molar ratio of Zn<sup>+2</sup>: OH<sup>-</sup> and different MW exposure time is observed by PL emission spectroscopy at room temperature, shown in Fig.6 and Fig.7.



**Fig.6** PL emission spectra of sample (a) M<sub>1</sub> (1:10),(b) M<sub>2</sub> (1:25) molar ratio.

Fig.6 shows the PL emission spectra of samples M<sub>1</sub> and M<sub>2</sub> prepared with varied molar ratio. A broad visible PL emission is observed centered on 477nm and 452nm corresponding to zinc interstitials (Zn<sup>••</sup>, Zn<sup>•</sup>) to valence band transition and 558, 531 nm corresponding to conduction to oxygen vacancy (V<sub>o</sub>) transition respectively [3]. The sample M<sub>1</sub> with 2D structure exhibits higher PL intensity as compare to M<sub>2</sub> which has a 1D structure. The phenomena of PL are a defect related phenomena [22-29]. The surface of Nanostructure contains defects, dangling bonds, vacancies etc. [30, 31]. The surface area is governed by the morphology of NPs. The ZnO nanosheets present a larger area and hence a larger number of defects present. This may be a possible explanation of higher PL intensity observed in 2D structure. Similar observations have been reported earlier too [12,32]. The ratio of intensities of blue to green emission is 1.88 for M1 and 1.65 for M2 respectively, which can be attributed to the change in defect concentrations responsible for defect emission.



**Fig.7** PL emission spectra of samples: (1) T<sub>1</sub> with 40 min MW exposure (2) T<sub>2</sub> with 10 min MW exposure.

The PL emission spectra of samples T<sub>1</sub> and T<sub>2</sub> are shown in Fig.7 showing a broad PL emission with lower intensities for sample T<sub>2</sub>. This can be easily related to the irregular nano crystals obtained in this case [33]. On the contrary for sample T<sub>1</sub>, the excitonic emission is observed at ~392 nm, due to higher crystallinity, purity and uniformity of the tiny ZnO NPs [12, 34]. The excitonic peak obtained in case of T<sub>1</sub> shows a red shift for T<sub>2</sub> which has bigger particle size.

## IV. Conclusion

The present study paves way to the size and shape controlled synthesis through a cost effective and green process, using pulsed MW irradiation. The MW aided process was rapid leading to uniform growth of 1D and 2D structures of ZnO NPs. This study explains a comprehensive growth mechanism responsible for change in morphology and structure through an analytical model. The MW exposure time effectively controls the particle size and shape. The excitonic peaks present in the room temperature PL spectra of some of the samples show that the as synthesized ZnO NPs exhibit superior optical properties.

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