Synthesis of ZnO Nanorods by Precipitation Method

S. S. Dange, S. N. Dange, P. S. More

Abstract: ***Zinc oxide nanorods were synthesized from zinc nitrate and ammonia solution by precipitation method assisted by microwave irradiation. The molarity of the bath solution was varied as 0.05M and 0.075M. The pH of the bath solution was varied as 7.5 and 8.0 for both the molarities and all samples were annealed at 250ºC. The nanorods were obtained from 0.075M zinc nitrate solution at pH 7.5. The structural and optical properties of the nanorods were characterized by X-ray diffraction (XRD), Scanning electron microscopy (SEM), and UV-Vis spectroscopy. The thermal characteristics was carried out by Thermo gravimetric and Differential thermal analyzer (TG-DTA) .The obtained nanorods shows length of 250-400 nm and diameter in the range of 45-60 nm. XRD pattern of ZnO nanorods shows hexagonal wurtzite structure with preferred (101) growth direction. The ZnO nanorods have UV absorption at 367.14 nm and the corresponding energy band gap is 3.37eV.***

Keywords: ***Zinc oxide, Precipitation method, Nanorods, Morphology***

I. INTRODUCTION

In recent years, nanosized semiconductors have received broad attention due to its remarkable electrical and optical properties useful in optoelectronic and electronic devices [1-3]. Zinc Oxide is one of the promising II-VI semiconductor with wide band gap of 3.37 eV and large exciton binding energy of 60meV at room temperature [4]. It has applications in the field of spintronics [5] , gas sensors [6], solar cells [7], photodetectors [8], and photocatalysts [9]. Besides it has a diverse group of growth morphologies such as nanowires, nanorings, nanobelts, nanorods, micro-almonds[10-14]. One dimensional (1-D) zinc oxide nanostructures such as nanorods, nanoneedles, nanoflakes [15,16] have attracted wide range of applications in nanodevices [3]. Various methods have been used to synthesize one dimensional ZnO nanostructures such as sol-gel, hydrothermal, microwave irradiation, chemical vapor deposition (CVD) and precipitation method [17-21]. Precipitation method is a solution phase method useful for the preparation of ZnO nanoparticles from aqueous solutions. It is a low cost and simple method. This method also allows to control the morphology, size and quality of crystallites by varying the solution pH, temperature and bath concentration [22].

In this work we have used precipitation method assisted by microwave irradiation to synthesis ZnO nanorods from zinc nitrate solution. Microwave irradiation helps in uniform and rapid volumetric heating [23].

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The molarity and pH of zinc nitrate bath solution was varied. Distinct nanorods like morphology of zinc oxide was obtained from 0.075 M zinc nitrate solution at pH 7.5 after annealing at 250ºC.

II. MATERIALS AND METHODS

Zinc nitrate ($Zn(NO_3)_2.6H_2O$) and ammonia solution were used as received without any further purification. The molarity of the zinc nitrate solution was varied as 0.05M and 0.075M. The zinc nitrate solution was kept under constant stirring using magnetic stirrer to dissolve the zinc nitrate completely. After complete dissolution of zinc nitrate, ammonia solution was added drop by drop under constant stirring to change the pH of the bath solution. The pH of the bath solution was varied as 7.5 and 8.0. The white precipitate formed was allowed to settle down. The precipitate was separated carefully and cleaned several times with distilled water and ethanol to remove the byproducts. Further it was kept in microwave oven on convection and microwave mode at 40ºC for 5 minutes. The obtained precipitate was annealed at 250ºC for two hours. The structural and optical properties of the prepared powder was characterized by X-ray diffractometer (Miniflex-II) with CuKα radiation (λ = 0.1540 nm) and UV-Vis spectrophotometer (SHIMADZU UV-1800). The analysis of the surface morphology was performed with a field emission scanning electron microscope (FESEM). Thermal analysis was carried out by using Rigaku Thermo plus TG 8120 thermal analyzer.

III. RESULTS AND DISCUSSION

1. X-Ray Diffraction (XRD)

The XRD pattern of the ZnO nanorods, given in Fig. 1, shows characteristic ZnO peaks which are in good agreement with the standard JCPDS data. The crystals have hexagonal wurtzite structure with prominent reflection peaks from (100), (002) and (101) planes. The lattice parameters were calculated from:

$$\frac{1}{d_{hkl}^2} = \frac{4}{3}\left(\frac{h^2+hk+k^2}{a^2}\right) + \frac{l^2}{c^2}$$

The values of the lattice parameters were found to be a = 3.252 Å and c = 5.214 Å.

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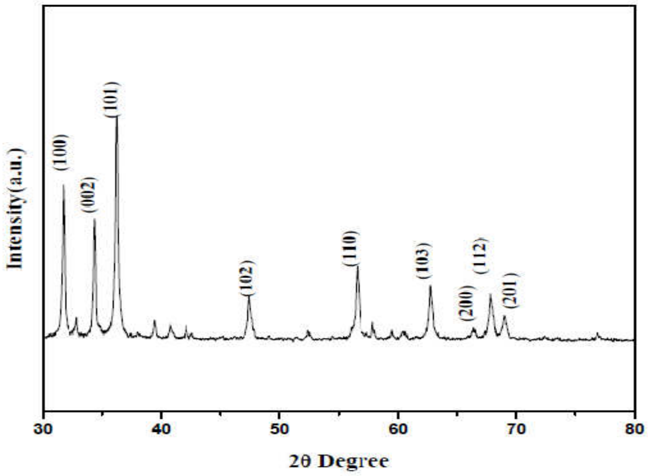

Fig. 1 : XRD pattern of ZnO nanorods

The crystallite size (D) was calculated from the most intense diffraction peak (101) using Debye-Scherrer's equation;

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

The average crystallite size is found to be 28.81nm. The micro-strain (ε) of crystallites for the most intense peak from (101) plane, was calculated by the following equation;

$$\varepsilon = \frac{\beta cos\theta}{4}$$

The micro-strain (ε) of the crystallites is found to be 0.0012.

2. *SEM*

SEM images in Fig. 2 shows morphology of ZnO nanoparticles for different molarity and pH of the bath solution. From Fig. 2(a) and 2(d) it is seen that for 0.05M and 0.075M zinc nitrate solution at pH 7.5 and 8.0 respectively, the ZnO crystallites have highly irregular and nonuniform morphology and size distribution. For 0.05M zinc nitrate solution at pH 8.0 ZnO crystallites shows irregular shapes but slightly uniform size distribution as seen from Fig.2(b). Fig.2(c) shows that for 0.075M zinc nitrate solution at pH 8.0 ZnO nanoparticles have distinct nanorod like morphology of approximate length 250-400 nm and diameter of about 45-60 nm.

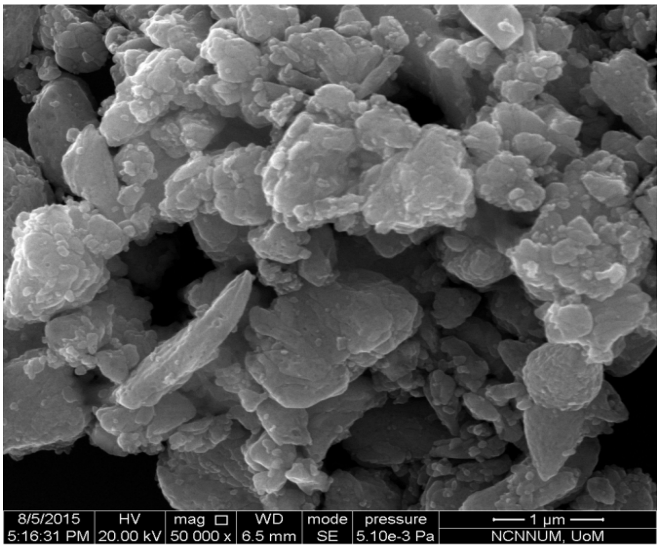

Fig 2(a) : Nanoparticles for 0.05M zinc nitrate at pH 7.5

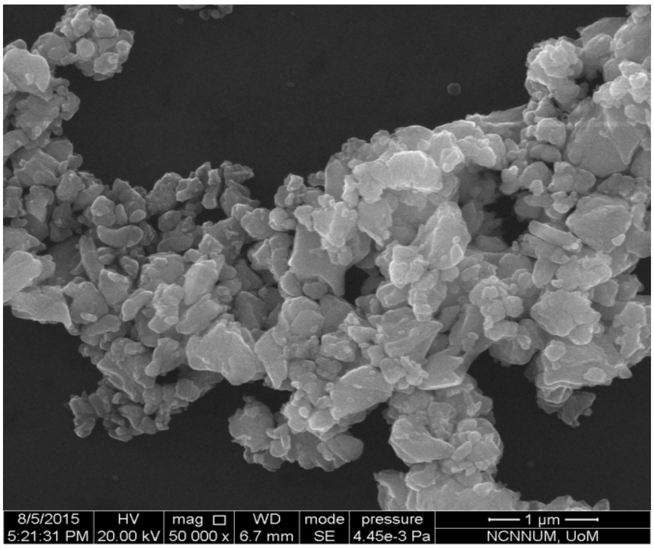

Fig 2 (b): Nanoparticles for 0.05M zinc nitrate at pH 8.0

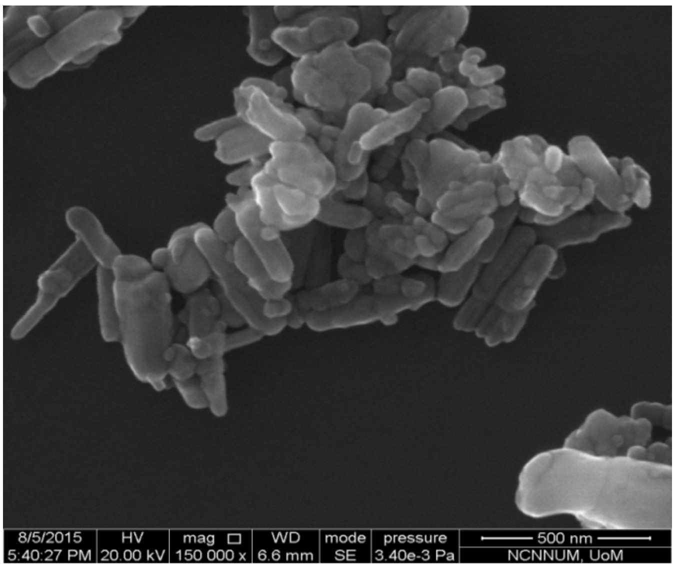

Fig 2(c): Nanorods for 0.075 M zinc nitrate at pH 7.5

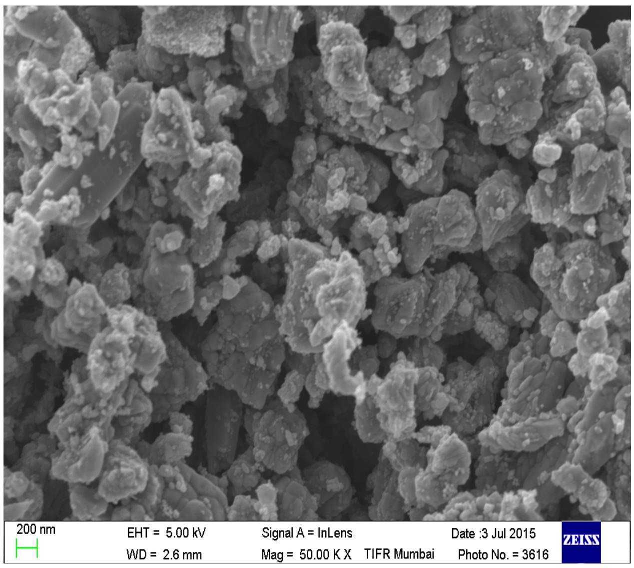

Fig 2 (d): Nanoparticles for 0.075 M zinc nitrate at pH 8.0

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3. *UV-Vis Absorption Spectrum*

UV-visible absorption spectroscopy was used to study the optical properties of ZnO nanorods.The absorption spectrum of ZnO nanorods is shown in Figure 3. The absorption peak is observed at 367.14 nm and the corresponding energy band gap is found to be 3.37eV.

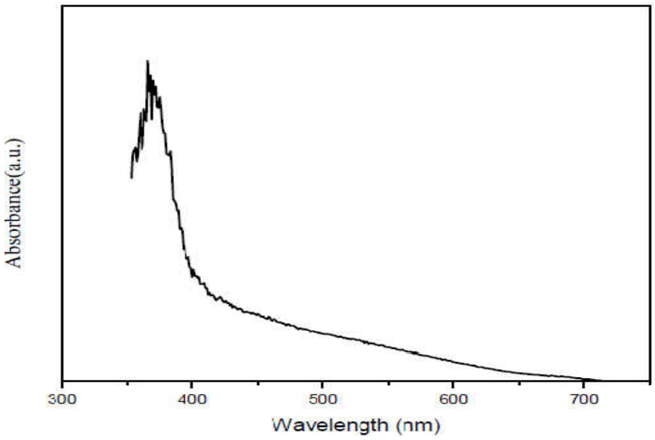

Fig. 3 : UV-vis absorption spectrum of ZnO nanorods.

4. *TG-DTA*

The thermal behavior of unannealed ZnO nanopowder corresponding to 0.075M zinc nitrate solution at 7.5pH was carried out at heating rate of 10ºC per minute in air atmosphere from room temperature to 900°C. The thermogram seen from Fig.(4) shows weight loss of 0.8 % , 2.88 % and 1.55 % between 26°C to 100°C , 100°C to 150ºC and 150ºC to 250ºC respectively. The observed weight loss is due to the evaporation of water and decomposition of residual organics. The endothermic peak is observed at 160ºC. The peak is accompanied by the weight loss. There was no further decomposition beyond 250ºC.

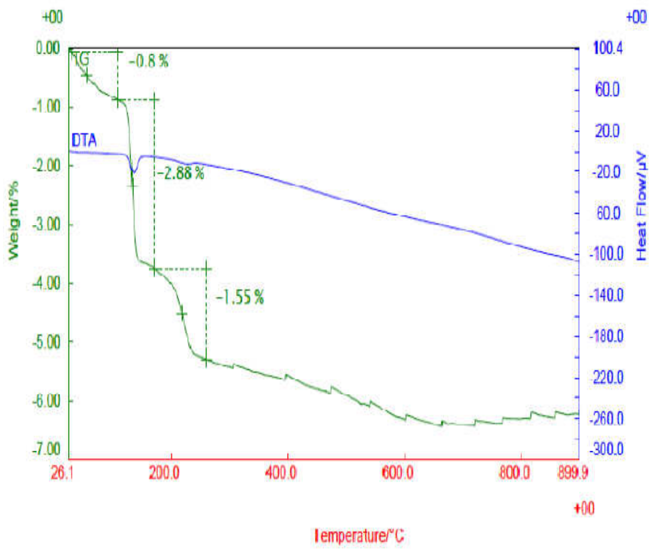

Fig. 4: TG-DTA curves for ZnO before annealing.

IV. CONCLUSION

Morphology study of ZnO nanoparticles at molarity 0.05 M and 0.075 M of zinc nitrate solution was carried out at pH 7.5 and 8.0. Microwave oven was used in combination of microwave and convection mode for 5 minutes at 40ºC to heat the precipitate. Distinct and uniform nanorods like morphology was observed for 0.075 M zinc nitrate solution at pH 7.5. The obtained nanorods are approximately 250-400nm in length and 45-60 nm in diameter. The ZnO nanorods shows UV absorption at 367.14 nm and energy band gap of 3.37eV, which might be of interest in nanoscale applications.

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