

Effect of pH on Morphology of Cu Added ZnO Nanostructures by Precipitation Method

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ABSTRACT: The influence of pH on the morphology of copper added zinc oxide (Cu at 5 wt%) nanostructures have been observed. The pH of the solution was varied as 7.5, 8.0 and 8.5. Distinct nanostructures like nanocapsules, nanospheres have been observed for these pH values. The structural and optical properties of the nanoparticles were characterized by X-ray diffraction (XRD), Scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR) and UV-Vis spectroscopy. XRD pattern shows that these ZnO nanoparticles have hexagonal wurtzite structure. The nanocapsules have approximate length of 250 nm and diameter of 45-60 nm . The nanospheres have approximate size of 100 nm. The prepared ZnO nanostructures shows UV absorption at 373.52 nm, 372.73 nm and 371.27 nm for pH 7.5, 8.0 and 8.5 respectively. The corresponding energy band gap for these nanoparticles are found to be at 3.319 eV, 3.326 eV and 3.339 eV.

KEYWORDS: Zinc oxide, precipitation method, morphology, nanostructures, nanocapsules

I. INTRODUCTION

In last few years , nanoscale zinc oxide material have received broad attention due to its remarkable properties useful in optoelectronic and electronic nanodevices[1, 2]. Zinc oxide (ZnO) is a semiconducting material with direct wide bandgap of 3.37 eV and large exciton binding energy of 60meV at room temperature [3]. It has a diverse group of growth morphologies such as nanowires , nanoring , nanobelts , nanorods , microalmonds [4-8] etc. Various methods have been used to synthesize ZnO nanostructures such as sol-gel, hydrothermal, microwave-assisted techniques, chemical vapor deposition (CVD) and precipitation methods [9-13].

Among these methods precipitation method is one of the solution phase method useful for the preparation of ZnO nanoparticles from aqueous solutions. The method allows us to control the morphology , size and quality of crystallites by varying the solution pH, temperature and bath concentration [14]. Microwave assisted synthesis has unique features such as uniform, rapid volumetric heating and high reaction rate. Rapid and controllable volumetric heating with a particular temperature distribution has effect on the structure and properties of the material[15].

In our experiment we have used precipitation method to synthesize copper added ZnO nanoparticles and microwave oven was used for heating purpose. The pH of the solution was varied as 7.5 , 8.0 and 8.5 by adding ammonia solution into the 0.075 M zinc nitrate solution. We have reported distinct morphology such as nanocapsules, nanospheres and irregular but uniform shapes for pH 7.5, 8.0 and 8.5 respectively.

II. MATERIALS AND METHODS

Zinc nitrate ($Zn(NO_3)_2 \cdot 6H_2O$), Copper nitrate ($Cu(NO_3)_2 \cdot 3H_2O$) and Ammonia solutions were used without further purification. Zinc nitrate solution was mixed with copper nitrate solution in the ratio 95% and 5% by weight to prepare 0.075 M Cu added zinc nitrate bath solution. The prepared solution was constantly stirred using magnetic

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stirrer at room temperature. The pH of the bath solution was varied by adding ammonia solution to it. The precipitate obtained in this process was separated and cleaned with distilled water and ethanol to remove the byproducts. It was further kept in microwave oven on convection and microwave mode at 40°C for 10 minutes. The precipitate was then annealed at 250°C for two hours. This prepared powder was characterized for structural and optical properties. X-ray diffraction pattern was recorded by using an X-ray diffractometer (Miniflex-II) of Cu K α radiation of wavelength $\lambda = 0.1541$ nm. Morphology of the prepared ZnO nanoparticles was studied by using scanning electron microscope SEM (ZIESS Ultra55 FESEM). The optical absorption spectra of the nanoparticles was recorded using a UV-VIS spectrophotometer (SHIMADZU UV-1800). FTIR spectra of the powder samples were recorded using Perkin Elmer spectrum 100 Fourier transform spectrometer in the range of 400 - 4000 cm⁻¹.

III. RESULTS AND DISCUSSION

1. X-Ray Diffraction (XRD)

Figure 1 shows the XRD pattern of Cu added zinc oxide nanoparticles at different pH of the solution. The peak position of all the XRD pattern are in good agreement with the standard JCPDS data for ZnO. The XRD pattern reveals that the crystals have hexagonal wuritze structure. A small negligible peak corresponding to CuO is observed for pH 7.5 and 8.0 indicating only a small mixture phase of CuO with ZnO.

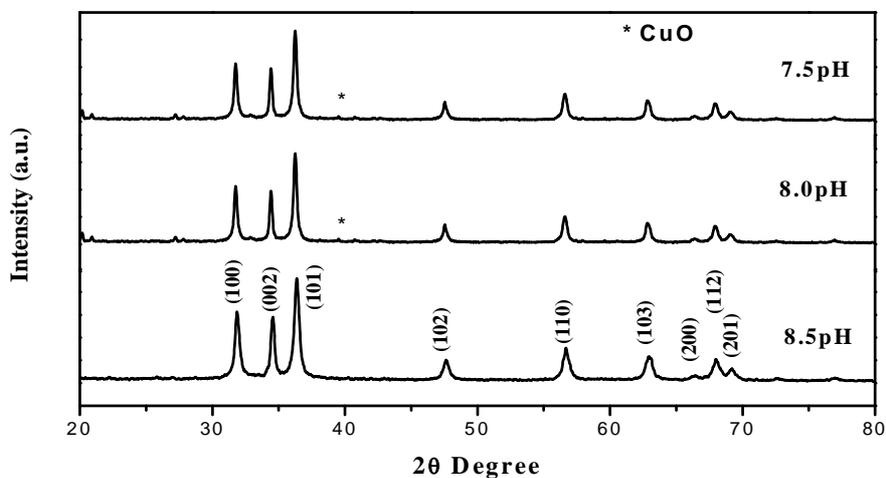


Fig.1 : XRD pattern for ZnO at different pH of solution.

The lattice parameters of the crystals shown in Table 1 are 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 average crystallite size (D) is calculated from the most intense diffraction peak (101) using Debye-Scherrer's equation;

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

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The micro-strain(ϵ) of crystallites for the most intense peak from (101) plane, shown in Table 1, are calculated by the following equation;

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

pH of solution	Crystalline size(nm)	Lattice constant		Micro-strain
		a=b(Å)	c(Å)	
7.5	23.21	3.248	5.206	1.49×10^{-3}
8.0	21.43	3.253	5.197	1.62×10^{-3}
8.5	17.41	3.244	5.183	1.99×10^{-3}

Table 1 : Crystalline size, lattice parameter and micr-strain of ZnO at different pH

From Table 1 it is seen that the values of lattice parameters shows no significant change for change in the pH of the bath solution as 7.5, 8.0 and 8.5. The average crystallite size is seen to remain same of about 20nm. The micro-strain of the crystallites is in the range 0.00149 to 0.00199.

2. SEM

SEM images of the Cu added zinc oxide nanostructures are shown in Figure 2(a), 2(b) and 2(c) for pH 7.5, 8.0 and 8.5. It is seen that the morphology of nanostructures strongly depend on the pH of the bath solution. At pH 7.5 capsule like structures of approximately 100-250 nm length and 45-60 nm in diameter is observed (fig 2(a)). Increasing pH value to 8.0 the crystallites show fairly uniform morphology of nanospheres having size of 50-100 nm, as seen in (fig 2 (b)). At pH 8.5 irregular shapes of size distribution in the range of 50-100nm have been observed, as seen in (fig 2(c)).

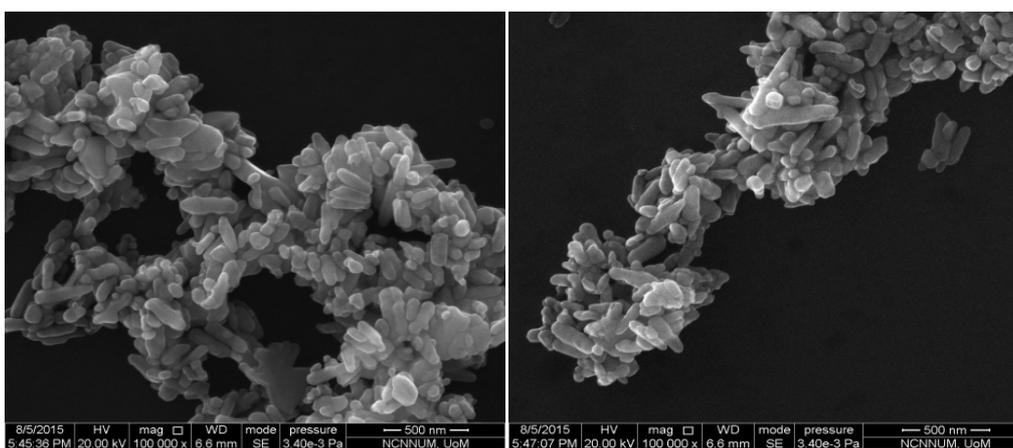


Fig. 2 (a) ZnO nanocapsules at pH 7.5

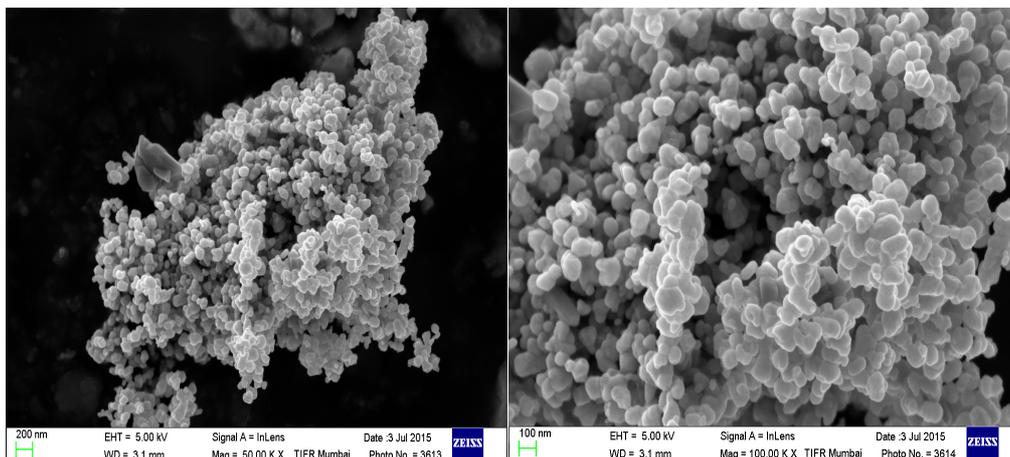


Fig. 2 (b) ZnO nanospheres at pH 8.0

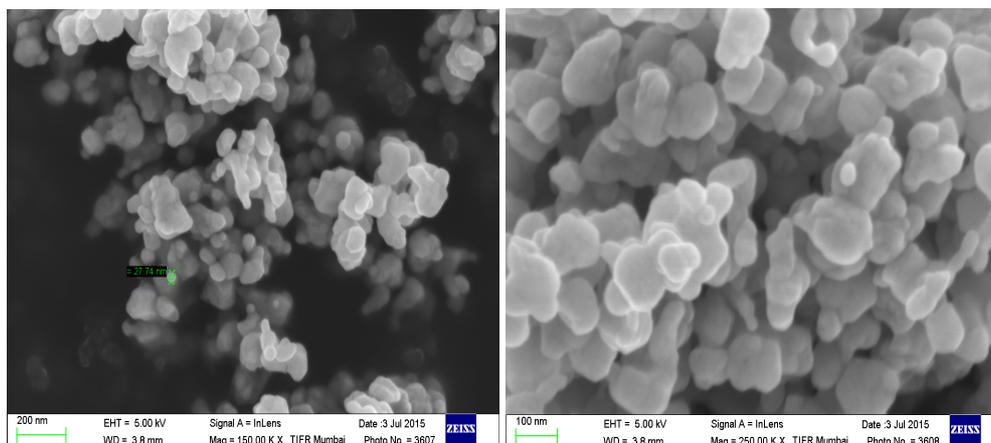


Fig. 2(c): Irregular shape of ZnO nanoparticles at pH 8.5

3. FTIR

Infrared absorption spectra of nanomaterials synthesized at different pH values are shown in Figure 3. Infrared absorbance spectra shows the vibration bands due to Zn-O bond, Cu addition and hydrogen bonding. For all pH values, strong absorption peaks in the range of $400 - 700 \text{ cm}^{-1}$ is observed due to ZnO stretching modes. An absorption peak around 1646 cm^{-1} is seen due to O-H bending mode of vibrations. Absorption peaks at 1390 and 1121 cm^{-1} corresponds to C-OH plane bending and C-OH out-of-plane bending, respectively. A broad band in the region $2900 - 3700 \text{ cm}^{-1}$ could be attributed to overlapping of physically absorbed water, O-H stretching modes and C-H stretching modes.

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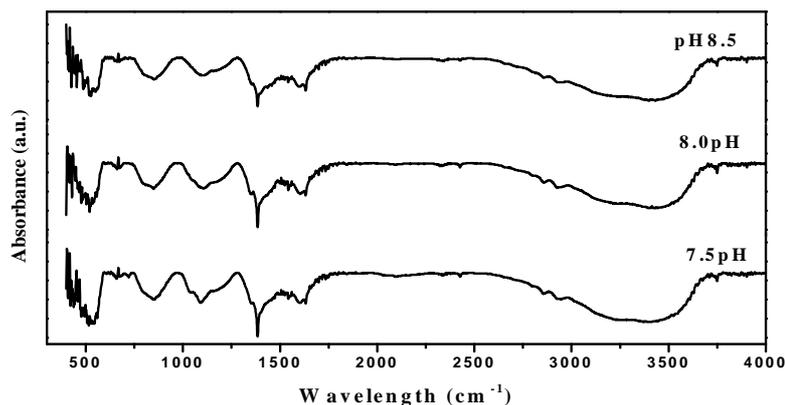


Fig. 3 : FTIR absorbance spectra for ZnO at different pH

From the FTIR spectra it is seen that there are no significant change in the absorption peaks due to the changes in pH values of the solution. The integrated absorption of the OH and CH stretching modes appears to be independent of the pH of the solution.

4 .UV-Vis Absorption Spectrum

To study the optical properties of nanosized particles, UV-visible absorption spectroscopy was used. The absorption spectrum of Cu added ZnO nanoparticles for various pH is shown in Figure 4. It exhibits absorption at 373.52 nm, 3.326 nm, 371.27 nm for pH 7.5, 8.0 and 8.5 respectively. The corresponding energy band gap for these nanoparticles are found to be 3.319 eV, 3.326 eV and 3.339 eV.

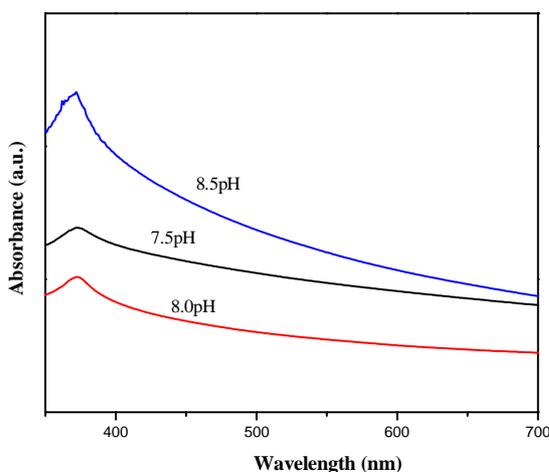


Fig 4 : UV absorption spectrum

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IV. CONCLUSION

Effect of pH on the morphology of Cu added ZnO nanostructures (Cu at 5 wt %) has been studied. The pH of solution significantly influences the morphology of the ZnO nanostructures. Distinct and fairly uniform morphology of ZnO nanostructures such as nanocapsules and nanospheres was observed for pH 7.5 and 8.0 of bath solution respectively. For pH 8.5 irregular shapes of nanostructures were observed. Further investigations are needed to design control parameters using changes in pH of bath solution to obtain desired morphology and size of nanoparticles for applications in nanotechnology.

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