Effect of pH values on surface Morphology and Particle size variation in ZnO Nanoparticles Synthesised by co-precipitation Method

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Abstract

Zinc oxide (ZnO) nanoparticles of size varying from 16 to 31 nm were synthesised by co-precipitation method using zinc acetate dihydrate ($Zn(CH_3COO)_2.2H_2O$) and sodium hydroxide (NaOH) as precursor materials. The pH value of solution was varied to study the surface morphology and particle size variations in ZnO. The X-ray diffraction peaks of all the samples corresponds to hexagonal wurtzite structure of ZnO and the data also shows significant variation in particle size as well as the lattice strain of ZnO nanoparticles with respect to pH values of the solution. The Scanning Electron Microscopy (SEM) images show different morphology at different pH values. Hexagonal shaped nanorod structures were observed at pH value of 7 and 9, and plate like structures were observed "at pH values 10.5 and 12.5. Fourier Transform Infrared Spectroscopy (FT-IR) confirms the formation of ZnO at ~450 cm^{-1}. UV-visible Spectroscopy (UV-vis) analysis shows symmetrical shift in the absorption edge towards the lower wavelength or higher energy region with decrease in particle size of the ZnO samples.

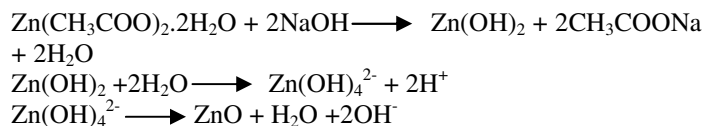**Keywords:** Zinc oxide, wurtzite, X-ray diffraction, Scanning Electron Microscopy, FT-IR.

Introduction

Zinc oxide (ZnO) is one of the most important II-VI semiconductor material with direct wide band gap (3.37 eV or 375 nm) and large exciton energy of 60 meV. This semiconductor has several favourable properties, including good transparency, high electron mobility, wide band gap, and strong room temperature luminescence[1,2]. ZnO exhibits the most splendid and abundant configurations of nanostructures that one material can form. ZnO has become an attractive inorganic material, owing to its unique properties and potential applications, electro and photo-luminescence devices, chemical sensors and so on[3-7]. The first requirement of any novel study of nanoparticles is the synthesis of the materials. The development of systematic studies for the synthesis of ZnO nanoparticles is a current challenge. Different techniques such as sol-gel, spray pyrolysis, thermal evaporation, wet chemical processes etc are used for the synthesis of ZnO nanoparticles. But co-precipitation method has proven to be the simple, fast and economic way of synthesising ZnO nanomaterials[8-10].

Material and Methods

Zinc acetate dehydrate ($Zn(CH_3COO)_2.2H_2O$) was procured from the Central drug house, Delhi and Sodium hydroxide (NaOH) was procured from Merck. All the chemicals used for the experiment were of analytical grade and used without further purification. MilliQ water was used throughout the experiment.

ZnO nanoparticles were prepared by simple co-precipitation method. In this typical synthesis procedure four different concentration of NaOH varying from 0.2 to 0.8 M was added drop wise to four replicates of 0.1 M $Zn(CH_3COO)_2.2H_2O$ solution and pH of all four final mixtures was measured. The precipitates was allowed to settle down, washed several times with MilliQ water and dried in hot air oven at 110° C for 6 hours. The powder so obtained was collected and used for further characterization. The chemical reaction for ZnO nanoparticles under precipitation condition at room temperature is described below:

$$Zn(CH_3COO)_2.2H_2O + 2NaOH \longrightarrow Zn(OH)_2 + 2CH_3COONa + 2H_2O$$
$$Zn(OH)_2 + 2H_2O \longrightarrow Zn(OH)_4^{2-} + 2H^+$$
$$Zn(OH)_4^{2-} \longrightarrow ZnO + H_2O + 2OH^-$$

Crystallite size (D), lattice parameter ('a' and 'c'), and average lattice strain (ε_{av}) of the sample were estimated by powder X-ray diffraction (Rigaku Miniflex) using Cu-K$_\alpha$ line (λ=0.15406 nm) with a scan speed of 3° per min over a 2θ range of 25-80°. The surface morphologies of all the samples were obtained by Field-Emission Scanning Electron Microscope (FESEM) (ULTRA 55 FESEM, Karl Zeiss). Different functional groups and structural features were analysed using Fourier Transform Infrared Spectrophotometer (FTIR) (Shimadzu, Prestige 21). The UV–visible absorption spectrum (Shimadzu, UV-2600) was recorded for optical characterization.

Results and Discussion

The pH values of all the solutions with respect to their NaOH concentration were measured with a digital pH meter and values were recorded. The typical powder XRD pattern of the ZnO nanostructures synthesised from precipitation method is shown in figure-1. The sharp intense peaks of ZnO confirms the high purity and good crystalline nature of ZnO and the peaks originated from (100), (002), (101), (102), (110), (103), (200), (112), (201), (004) and (202) represents the hexagonal wurtzite structure of ZnO as per JCPDS (card no. 01-79-0206) standards[8]. The lattice parameters 'a' and 'c' calculated were also in accordance with the reported value. The average grain size of the samples was estimated with the help of Debye Scherrer equation.

$$D = \frac{0.94\,\lambda}{\beta\cos\theta} \tag{1}$$

Where λ is the wavelength (Cu Kα), β is the full width at the half-maximum (FWHM) of the ZnO (101) peak and θ is the diffraction angle. It has been observed that the average grain size calculated by equation 1. showed decreasing trend from 31 nm to 16 nm as the pH increases from 7 to 12.5. It has been observed that the FWHM of the peaks were inversely proportional to crystallite size, which indicates better crystalline quality with respect to crystallite size of ZnO.
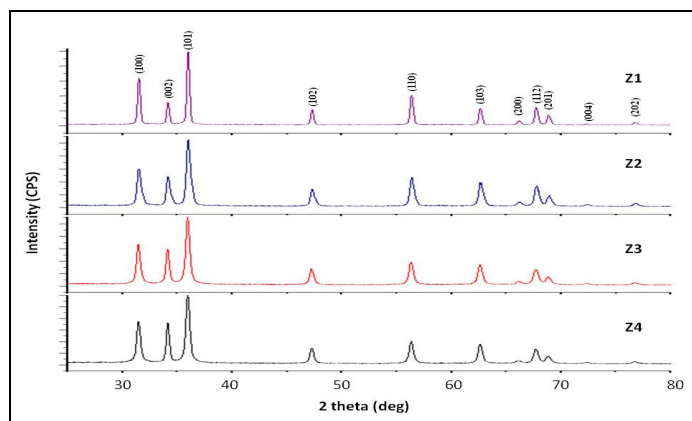

Figure-1
X-ray diffraction patterns with (hkl) values of ZnO nanoparticles synthesised by co-precipitation method with different pH values

The lattice strain (ε_{av}) has been calculated using tangent formula (equation 2). The calculated results show significant increase in the lattice strain associated with the reduction of crystallite size of ZnO. The graph between average lattice strain and particle size is shown in figure 2. The obtained results are in agreement with the work carried out by Muhammad et al[11]. The variation in the particle size, lattice constants 'a' and 'c' and average lattice strain corresponding to different pH values were tabulated in table-1.

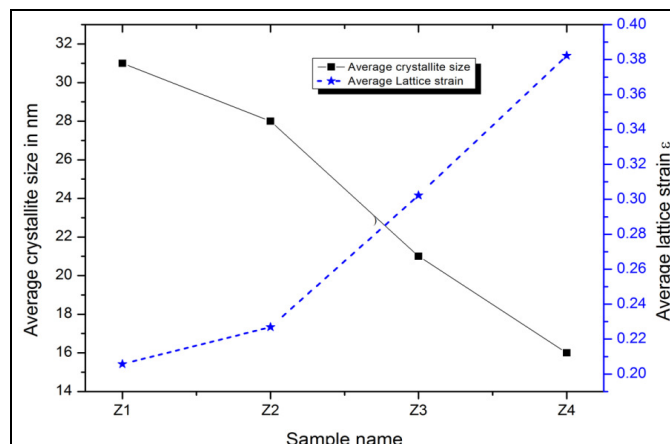$$\varepsilon_{av} = \frac{\beta}{4\tan\theta} \tag{2}$$

Figure-2
Variation in average crystallite size (D) and average lattice strain (ε_{av}) with samples of different concentration of NaOH

The surface morphology of all the samples were characterised using FESEM. All the images show the formation of different surface morphology with respect to the samples. The figure 3(a) shows typical hexagonal rod like ZnO nanostructures corresponding to the sample Z1. The deformation of hexagonal rod like structures was observed in sample figure 3(b) which corresponds to sample Z2. The formation of plate like structures of sample Z3 and Z4 were observed in figure 2 (c) and 2 (d) respectively. The variation in the surface morphology of the samples is attributed to the lattice mismatch, chemical bonding across the interface and presence of residual oxides[12].

FTIR analysis was done by mixing ZnO sample with potassium bromide (KBr) in open air atmosphere. The significant absorption peaks near ~3350, ~1550, ~1400 and ~450 cm^{-1} can be noticed from the spectrum (figure 4). The strong absorption peak at ~450 cm^{-1} represents the Zn-O stretching frequency[13,14]. The broad peak near ~3350 cm^{-1} suggests the presence of the hydroxyl group (O-H)[14]. The weak bands near ~1550 cm^{-1} and ~1408 cm^{-1} represent C=O and C-O stretch respectively[15,16].

Table-1
Structural information on ZnO nanoparticles grown with respect to the pH of the solution by co-precipitation method

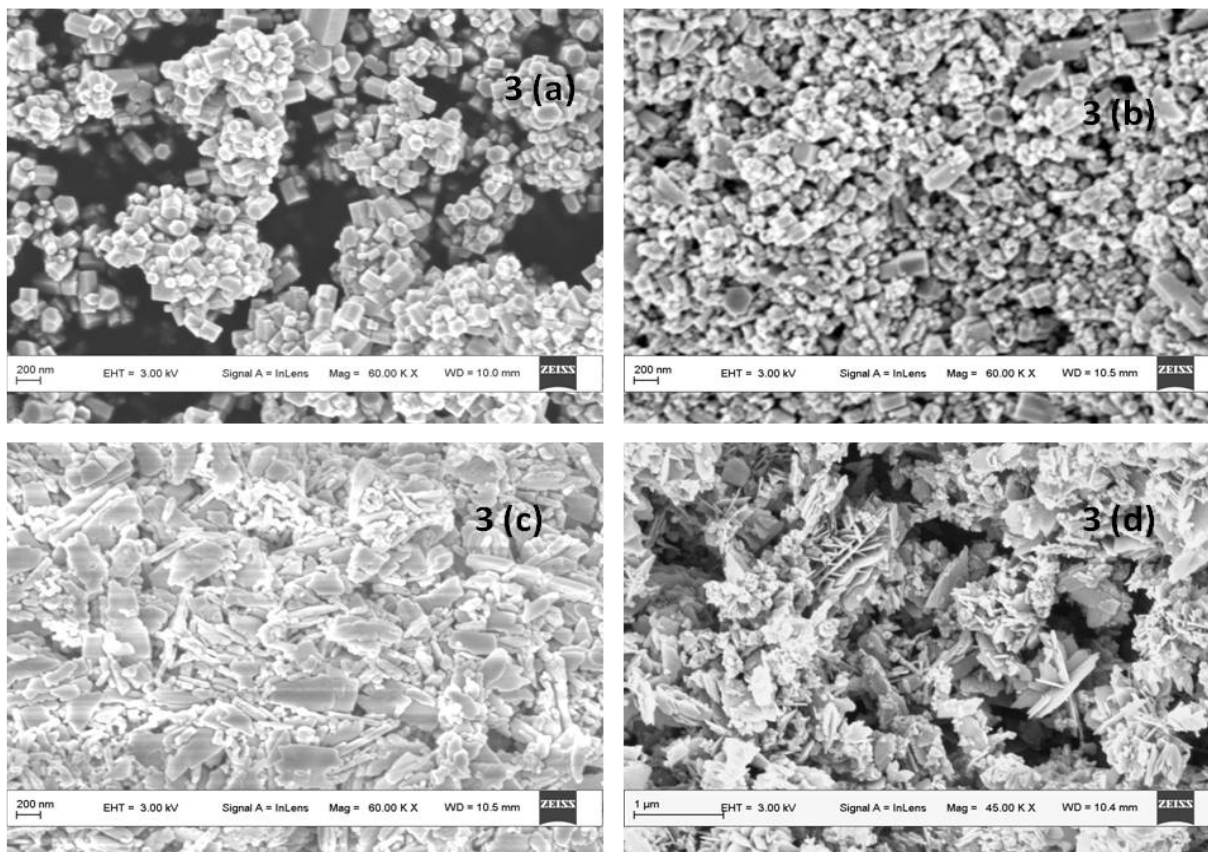| Sample name	pH	2 θ	FWHM 'β'	Crystallite size 'D' in nm	Lattice parameters		Lattice strain in %
					'a' in nm	'c' in nm	
Z1	7	35.95	0.2670	31	0.2884	0.4992	0.3591
Z2	9	35.85	0.2936	28	0.2892	0.5005	0.3960
Z3	10.5	35.92	0.3920	21	0.2886	0.4996	0.5277
Z4	12.5	36.04	0.4975	16	0.2877	0.4980	0.6673

Figure-3
FESEM images of the ZnO nanoparticles based on the pH. (a) at pH 7 (b) at pH 9 (c) at pH 10.5 (d) at pH 12.5.
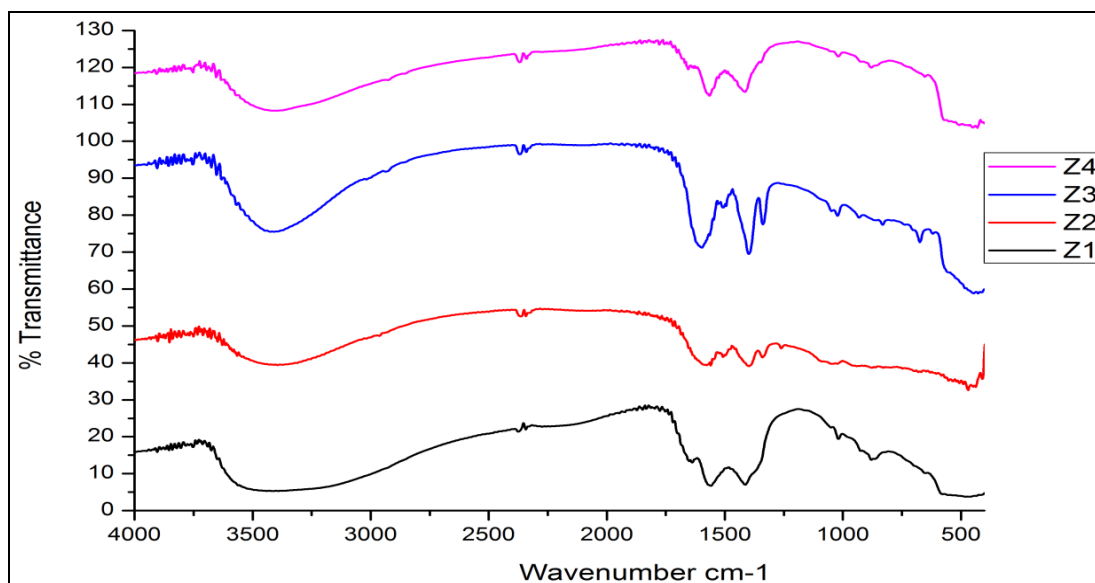

Figure-4
FTIR spectrum of ZnO nanoparticles with respect to the pH values

Figure 5 shows the UV-Visible absorption spectra of the nanostructures with a sharp excitonic absorption speak around ~368 nm. It is clear that the absorption edge systematically shifts to the lower wavelength with decreasing size of the nanoparticles[17].
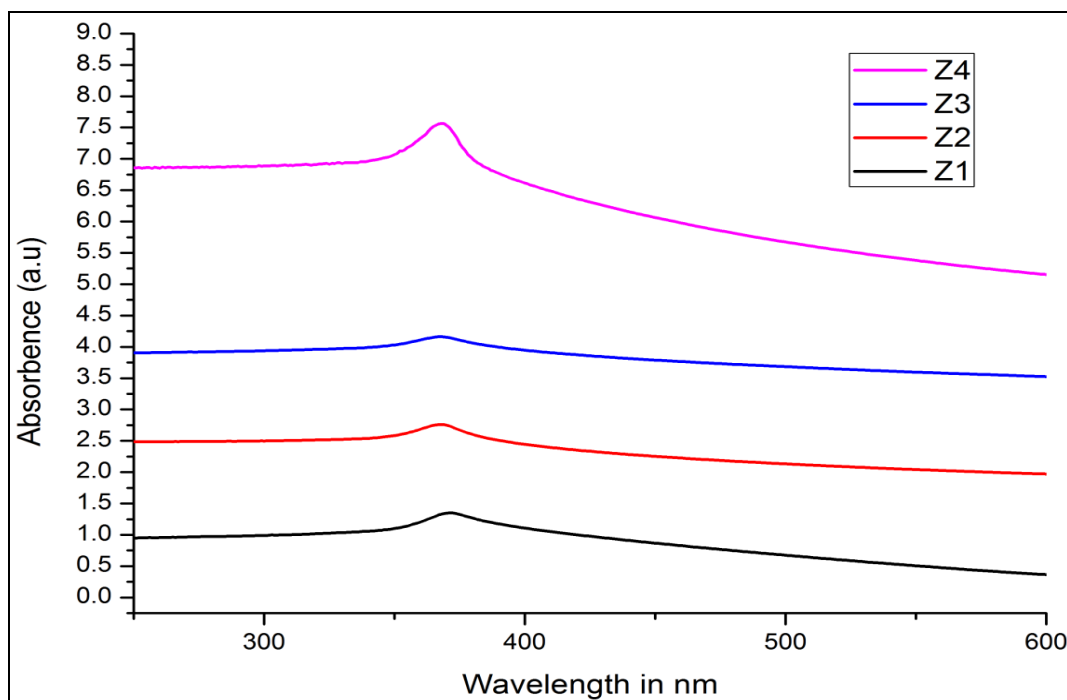
Figure-5
UV-Vis spectrum of ZnO nanoparticles with respect to the pH values

Conclusion

Highly crystalline and pure ZnO nanoparticles of different structures were successfully synthesised by simple co-precipitation method. The grown nanostructures were characterised by powder XRD, FESEM, FTIR spectroscopy and UV-Vis absorption spectroscopy. The powder XRD analysis confirms the hexagonal wurtzite structure of the ZnO nanoparticles and the sharp exitonic peaks suggests the high crystallinity of the ZnO nanocrystals. Also the decrease in the particle size is observed with increase in the pH of the solution. The average lattice strain (ε_{av}) increased with decrease in crystallite size of the ZnO nanoparticles. The FESEM images showed different surface morphology with respect to pH. The FTIR analysis reveals the characterization peaks of Zn-O stretching. The blue shift observed in the UV–Vis spectrum is the typical signature of size confinement in ZnO nanocrystals [15]. Variation in pH value has played crucial role in tailoring the crystallite size as well as different morphology of the ZnO nanoparticles.

Acknowledgement:

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