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Influence of pH on Structural Morphology of ZnO Nanoparticle

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Abstract: ZnO nanoparticles were prepared by solvothermal method by varying two different pH under harsh condition. Morphological change in ZnO nanoparticles from nanosphere to nanorods on varying pH from 11.0-10.7 was observed in Scanning Electron Micrograph (SEM). And also, the size of ZnO nanoparticle formed at 11.0 pH was found to be 54 nm. The XRD patterns of ZnO nanoparticle showed polycrystalline nature of ZnO nanoparticle. FTIR peaks at 548 and 555 cm^{-1} confirmed the presence of ZnO nanoparticle formation. Again UV-visible absorption spectra showed cut off wavelength at 416 nm which revealed that the size of ZnO nanoparticles were in nanodimension.

Key words: ZnO nanoparticle, solvothermal method, polycrystalline

INTRODUCTION

Nowadays metal oxide powders are very popular in gas sensor (Sivalingam *et al*., 2011) and biosensor. Especially nanosized metal oxide powders are preferable because nanodimensional feature enhances surface area and conductivity. ZnO nanoparticles are attracted a lot nowadays due to its wide application in optoelectronics and sensors. ZnO nanoparticle exhibits different morphology which depends on varying parameter such as temperature, pH and synthesis method (Shakti *et al*., 2011). Solvothermal method, spray pyrolysis and thermal decomposition are some of commonly used methods to synthesize ZnO nanopowders (Hsieh, 2007). Solvothermal method is very simple and easy to prepare ZnO nanoparticle when compared to other synthesis method. Due to this reason, in this study solvothermal method was chosen to synthesis ZnO nanorods. Temperature is another important variable parameter, plays a major role in determining size of ZnO nanopowders. Generally rate of reaction gets increased on increasing temperature more than the temperature needed for the rate of reaction to happen. Hence, a low temperature must be maintained constantly throughout the entire reaction for well defined controlled nanostructures. In this study, influence of pH on structural morphology of ZnO nanoparticle was investigated. ZnO nanoparticle. Under strong acidic condition or strong basic condition, ZnO powder's structural morphology can be controlled to nanodimension. This is due to the presence of more accumulation of charges surrounding ZnO nanoparticle. In the present study, the ZnO nanoparticle formation at two different pH 10.7 and 11.0 was investigated.

MATERIALS AND METHODS

Zinc acetate dehydrate ($Zn(CH_3COO)_2.2H_2O$) was purchased from Sigma-Aldrich, USA and methanol (CH_3OH) was purchase from fisher scientific, Mumbai. Methanol was procured from Merk India Ltd., India. procured from Merk India Ltd., India.

Synthesis of ZnO nanoparticle: ZnO nanoparticles were synthesized from precursor zinc acetate dihydrate. Initially 0.1 M of zinc acetate dihydrate was dissolved in 50 mL methanol. The above mixture was stirred constantly for 5 min. 0.3 M of NaOH was added to the above prepared stock solution in order to get pH value 10.7 and 11.0, respectively. These solutions were kept in hot air oven at 100°C for 6 h. After 6 h, the white colored product was allowed to dry at room temperature. Finally, the white colored products was washed with methanol, filtered and dried at 60°C.

RESULTS AND DISCUSSION

SE micrographs of ZnO powder samples at pH 10.7: SE micrographs of ZnO powder samples prepared at pH 10.7 are shown in Fig. 1. From SE micrographs, many agglomerated ZnO nanorod structures along with few

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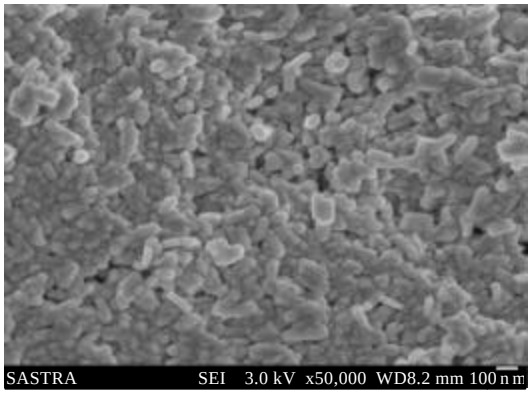

Fig. 1: SE micrographs of ZnO powder samples prepared at pH 10.7

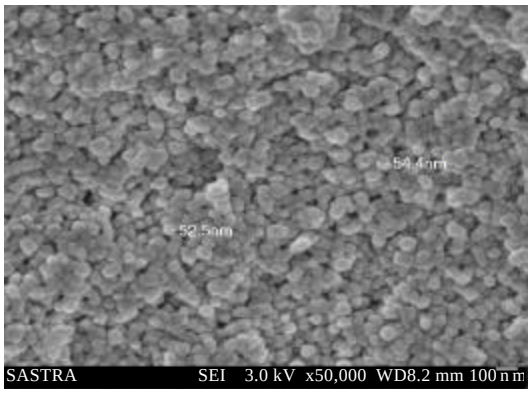

Fig. 2: SE micrographs of ZnO powder samples prepared at pH 11

nanospheres were observed. The preferential growth was may be due to more accumulation of charges around ZnO nanoparticle. This rod type morphology has high surface area when compared to sphere type morphology.

SE micrographs of ZnO powder samples prepared at pH 11: SE micrographs of ZnO powder samples prepared at pH 10.7 are shown in Fig. 2. The ZnO powders were found to have homogenous distribution of ZnO nanospheres with uniform size around 54 nm. It was also observed that the morphology of ZnO nanoparticle changes from nanorods to nanosphere on increasing pH from 10.7-11. But the surface area was found to be decreased due to its spherical morphology.

XRD pattern of ZnO powder samples prepared at pH 10.7: XRD pattern of ZnO powder samples prepared at pH 10.7 are shown in Fig. 3. From the XRD profile of ZnO powder samples, the obtained diffraction peaks were (100), (002), (101), (102), (110), (103) and (112).

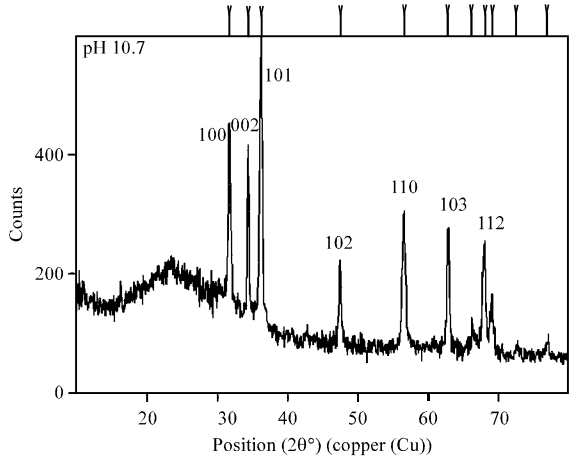

Fig. 3: XRD pattern of ZnO powder samples prepared at pH 10.7

Table 1: Peak list details of XRD pattern of ZnO powder samples prepared at pH 10.7

Position (2θ°)	Height (counts)	FWHM (2θ°)	d-spacing (Å)	Rel. Int. (%)
31.73	193	0.4	2.81767	56.83
34.406	204	0.2	2.60446	60.13
36.23	339	0.4	2.47760	100.00
47.51	102	0.4	1.91225	30.19
56.58	131	0.5	1.62535	38.73
62.85	173	0.3	1.47736	51.10
66	4	1.0	1.41101	1.09
68.0754	130.22	0.1968	1.37732	38.43
69.12	41	0.13	1.35790	12.05
72.58	14	0.14	1.30146	4.22
77.0	23	0	1.23777	6.76

Å: Angstrom (10^{-10} m), FWHM: Full width half maximum, Rel. Int.: Relative intensity

This confirmed polycrystalline nature of ZnO powder samples. Indexed peaks of XRD pattern of ZnO nanopowders prepared at pH 10.7 are given in Table 1. From this data set the distance between two lattice planes was found to be 2.4776 Å. The higher FWHM of 0.4 degree at 36.23 degree indicates the increased size of ZnO nanorods. The relative intensity of the diffraction peak at 34.447 degree was found to be sharp and having higher intensity which indicated that large quantity of ZnO nanorods were observed.

XRD pattern of ZnO powder samples prepared at pH 11: XRD pattern of ZnO powder samples prepared at pH 10.7 are shown in Fig. 4. When XRD profile of ZnO powder sample prepared at pH 10.7 was compared to XRD profile of ZnO powder sample prepared at pH 11, crystallinity of ZnO powder sample prepared at pH 11 got slightly decreased. This was due to the exposure of ZnO nanoparticles towards extreme pH. The diffraction peaks were (100), (002), (101), (102), (110), (103) and (112)

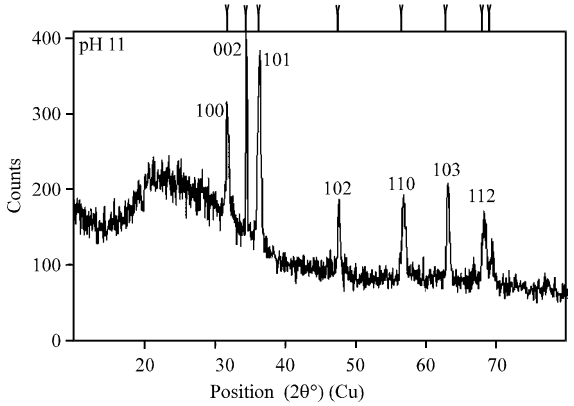

Fig. 4: XRD pattern of ZnO powder samples prepared at pH 11

Table 2: Peak list details of XRD pattern of ZnO powder samples prepared at pH 11

Position (2θ°)	Height (counts)	FWHM (2θ°)	d-spacing (Å)	Rel. Int. (%)
31.76	91	0.39	2.81476	46.69
34.447	194	0.17	2.60146	100.00
36.27	141	0.46	2.47461	72.79
47.52	53	0.40	1.91175	27.43
56.62	74	0.60	1.62414	38.22
62.86	102	0.36	1.47712	52.53
68.0	42	0.50	1.37750	21.69
69.1	35	0.30	1.35884	17.85

Å: Angstrom (10^{-10} m), FWHM: Full width half maximum, Rel. Int.: Relative intensity

confirms polycrystalline nature of ZnO nanospheres. Grain size of ZnO powder sample was calculated using Debye's Scherrer equation:

$$\text{Grain size} = \frac{K\lambda}{\beta\cos(\theta)}$$

Where:

β = 0.17 (degree)
λ (lambda) = 1.5406×10^{-10} m,
θ = 34.447 (degree) and
K = 0.9

From Scherrer equation, crystallite size of ZnO powder sample was calculated to be about 47.63 nm. Mismatch between estimated size of ZnO nanoparticle obtained from SEM and XRD was observed.

Indexed peaks of XRD pattern of ZnO nanopowders prepared at pH 11 are given in Table 2. From this data set the distance between two lattice planes was found to be 2.6014 Å. The small FWHM of 0.17 degree at 34.447 degree indicates the increased size of ZnO nanorods. The relative intensity of the diffraction peak at 34.447 degree was found to be sharp and having higher intensity which indicated that large quantity of ZnO nanospheres were observed.

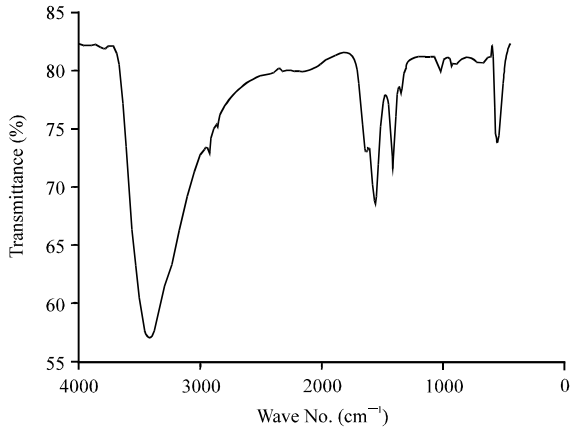

Fig. 5: FTIR spectra of ZnO powder sample prepared at pH 10.7

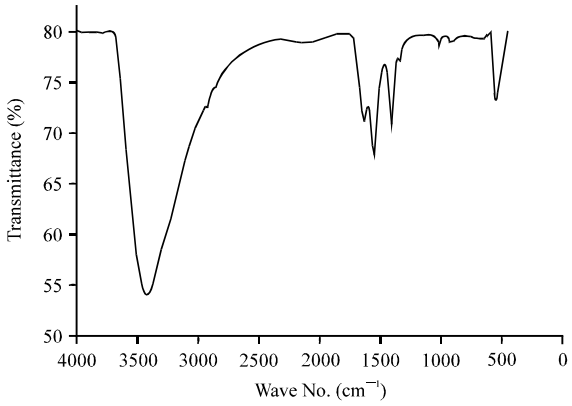

Fig. 6: FTIR spectra of ZnO powder sample prepared at pH 11

FTIR of ZnO powder samples: FTIR spectra of ZnO powder samples prepared at two different pH 10.7 and 11.0 concentrations are shown in the Fig. 5 and 6, respectively. Peak at 548 and 555 cm^{-1} confirmed the presence of ZnO nanoparticle formation. In addition to these impurities were also observed along with zinc oxide nanoparticle.

UV-visible absorption studies of ZnO nanorods: Figure 7 shows UV-visible absorption spectrum and 2dUV spectrum of ZnO nanoparticles prepared from zinc acetate precursor which was obtained by dispersing ZnO nanoparticles on glass slide. An absorption peak at 396 nm showed that the size of ZnO nanoparticles was in nanodimension. There is a simple method to calculate band gap energy from value of ZnO nanoparticles in powder form using UV/Vis/NIR spectrometer (Dharma and Pisal, 2009):

$$\text{Band gap energy } (E) = hc\lambda$$

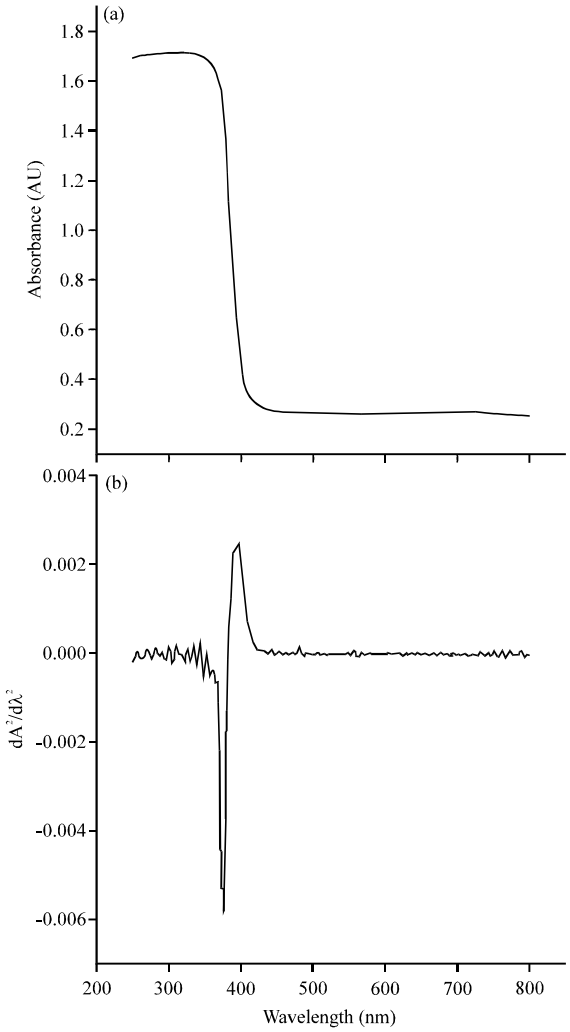

Fig. 7(a-b): (a) UV-visible absorption spectrum and (b) Second order of UV spectrum of ZnO nanoparticle prepared at pH 10.7

Where:

h = 6.626×10^{-34} Joule Sec (planks constant)
c = 3.0×10^{8} m sec^{-1} (speed of light)
λ = 416.57×10^{-9} m (cut off wavelength) and
1 eV = 1.6×10^{-19} Joule (Conversion factor)

The band gap energy for ZnO nanoparticles in powder form was found to be 2.9824 eV.

Grain Size of ZnO nanoparticles can be estimated from the peak absorbance wavelength. The following equation describes the particle size as a function of peak absorbance wavelength for ZnO nanorods:

$$r(nm) = \frac{-0.3049 + \sqrt{-26.23012 + \frac{10240.72}{\lambda_p(nm)}}}{-6.3829 + \frac{2483.2}{\lambda_p(nm)}}$$

where, λ_p is 396 nm (peak absorbance wavelength) and r represents radius of ZnO nanoparticles (Kumbhakar *et al*., 2008). The particle diameter of ZnO nanoparticles calculated using the above equation was found to be 12.1256 nm.

CONCLUSION

Polycrystalline nature of ZnO nanoparticle was observed in both ZnO powder samples prepared at pH 10.7 and 11.0. Change in structural morphology from nanospheres to nanorods was observed on varying pH from 11-10.7. This nanorods was found to be having high surface area, when compared to nanospheres. This high surface area makes ZnO nanorods a suitable sensing element for sensing biomolecule and toxic gases.

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