Grain Size Dependent Photo Luminescent Studies on Nanostructured Zinc Oxide

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Abstract: ZnO nanoparticles were synthesized using chemical precipitation technique. The characterization of the sample was done using XRD and optical study was done using PL spectra. From XRD it was found that the grain size decreased with increase in pH. The PL spectra exhibited excellent fluorescent characteristics of ZnO. The average bandgap of ZnO nanoparticles were also calculated at different excitation wavelengths. Comparative study of ZnO samples were done by varying pH and temperature. Vibrational spectra of the nanoparticles were recorded in the range 400-4000 cm-1. The peaks of ZnO nanoparticles annealed at higher temperature were found to be weaker compared to those annealed at lower temperature.

Keywords: nanomaterials, vibrational spectra, zinc oxide

1. INTRODUCTION

Nanotechnology and nanoscience are broad and interdisciplinary areas of research and development activity that have been growing explosively world wide during the past several years. It has the potential in revolutionizing the ways in which materials and products are created and the range and nature of functionalities accessed [1]. It is an interdisciplinary science that involves physics, chemistry, mathematics, and life sciences in particular genomics and proteomics. A nanometer is 1 billionth of a meter. In simple terms nanotechnology can be defined as engineering at very small length scales. Design, fabrication and application of nanostructures or nanomaterials and the fundamental understanding of the relationships between physical properties and materials dimensions characterize the fields of nanotechnology and nanoscience [2].

Nanostructured materials are materials with morphological features on the nanoscale, and especially those which have special properties stemming from their nanoscale dimensions [3]. When the dimension of a material is continuously reduced from a large macroscopic value to a very small size, the properties remain the same at first and then changes begin to occur. When the size drops below 100 nm, dramatic changes in properties can take place. If one dimension is reduced to the nanometer range while the other two dimensions remain large, the obtained structure is a quantum well. Two dimensional materials such as thin films and other engineered surfaces are examples. If two dimensions are reduced and one dimension remains large, the resulting nanostructure is referred to as a quantum wire. Quantum wires include carbon nanotubes, nanowires, whiskers, etc. The limiting case of this process of size reduction is when all the three dimensions reach nanometer range. This process produces quantum dots. Fullerenes, dendrimers and other nanoparticles fall in this category.

Knowledge of variations in the properties of nanoparticles with particle size is important to the fundamental understanding of these systems and is also useful in a variety of technological applications. Spatial confinement can in general affect a property when the size of the system becomes comparable to or smaller than a critical length scale for the mechanism that is responsible for that property. The uniqueness of nanoparticles lies in its large surface to volume ratio. As the particle size decrease the spectral indicators and the characteristics of the surface atoms or ions become increasingly dominant. Also in nanostructured materials, when the crystal size is reduced to a few nanometers the average density and the coordination between the nearest neighbors are changed. As a result, the properties of these materials become different from those of bulk crystals.

Zinc oxide (ZnO) is a well-studied representative of II-VI class of semiconductors. It has a unique position among semiconducting oxides due to its piezoelectric and transparent conducting properties [4]. It has a wide band gap of 3.37 eV and large exciton binding energy of 60 meV. It has high electrical conductivity and optical transmittance in the visible region. These properties make it an ideal candidate for applications like transparent conducting electrodes in flat panel displays and window layers in solar cells. ZnO has applications in areas such as laser diodes, solar cells, gas sensors, and optoelectronic devices. It has a crystalline wurtzite structure, shown in Fig. 1.

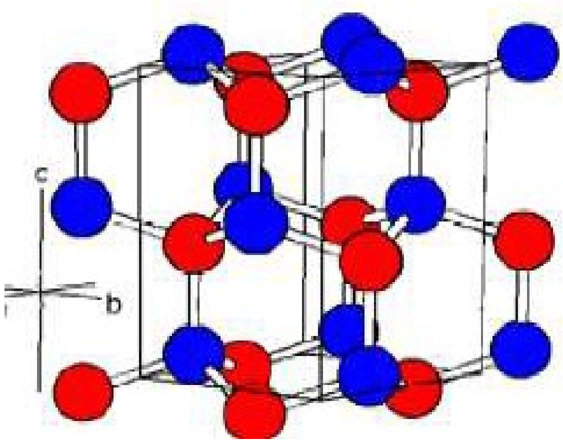

Fig.1: Wurtzite structure of zinc oxide (ZnO)

Experimental

Nanoparticles of $ZnCO_3$ were synthesized through controlled chemical reaction between solutions containing Zn^{2+} and CO_3^{2-} in presence of EDTA as the stabilizer. The reaction is $Na_2CO_3 + Zn(NO_3)_2 \rightarrow ZnCO_3 + 2Na(NO_3)$.

0.1Normal (N) Na_2CO_3 and 0.1N $Zn(NO_3)_2$ were taken in two conical flasks and were mixed with 100ml distilled water. Using two dropping funnels, the compounds were allowed to fall drop by drop into a vessel of 0.01N EDTA solution. The synthesis was carried out with the reaction mixture under constant stirring. The white gel like precipitate of nanoparticle $ZnCO_3$ was filtered, washed with distilled water and acetone several times to remove the impurities. $ZnCO_3$ sample was annealed at different temperatures to obtain samples of ZnO of different grain size. Five samples were prepared by changing the pH of the precursors, annealing temperature, etc. The sample codes, annealing time and temperature are given in the table below:

Sample code	pH	Annealing temperature (^0C)	Annealing time (minutes)
S1	10	250	15
S2		300	15
S3		400	15
S4	8	300	15
S5		400	15

Table.1. ZnO nanoparticles synthesized by changing the pH of precursors and annealing temperature

RESULTS AND DISCUSSION

X ray diffraction patterns of nanoparticles of ZnO synthesized by changing the pH of the precursors and annealing temperature are shown in Fig.2 and Fig.3. Grain size (t) of each sample was calculated using Scherrer formula [5]

$$t = k\lambda/\beta\cos\theta \;\;\ldots\ldots\ldots\ldots(1)$$

where k is a constant, λ is the wavelength of x –ray used, β is the full width at half maximum, θ is the scattering angle. The grain sizes calculated for the different samples are given in Table 2. They range from 12 to 24 nm.

A comparative study of ZnO nanoparticles synthesized by annealing at same temperature 300^0C and 400^0C but by varying pH was done. It was found that the grain size decreased with increase in pH. It is listed in the Table 3. The d spacing of each peak are calculated and listed with the X-Ray Diffraction (Fig.4). It revealed that the peaks of all the samples were consistent with the standard X-Ray Diffraction values of ZnO with Hexagonal structure (ICDD-79-0205). The plane of reflection of each peak can be determined using the standard X- Ray diffraction values. The hkl values are consistent with the standard values of ZnO.

The material ZnO shows fluorescence. From the photoluminescence spectra (Fig. 5-8) it is seen that the ZnO nanoparticles are effective fluorescent materials. The emission wavelength and intensity of the nanoparticles are listed in Table (4-7). The ZnO samples have fluorescent emission with wavelength between 380 nm to about 570 nm. This is in the visible region (380 nm to 750 nm). The main peaks of the emission spectra are at a wavelength of 465 nm (blue region 450 nm to 495 nm) and 448 nm (very near to the blue region). The excitation wavelengths are in the UV region. At excitation wavelength 360 nm, resonance fluorescence begins and they have high intensity at the excitation wavelengths 365 nm and 370 nm. At the excitation wavelength 365 nm, a peak with small intensity occurs with wavelength 730 nm (double of 365) and at 370 nm a peak with high intensity occurs with wavelength 740 nm (double of 370 nm). The intensity of all the peaks for the sample S5 (23.92 nm) is greater than the corresponding intensity of emission of sample S1 (12.66 nm). From the UV-Visible studies the average bandgap values corresponding to different excitation wavelengths were obtained and are listed in Table 8.

Fourier Transform Infrared Spectroscopy (FTIR) spectra of nanoparticles of ZnO (S1 and S2) at two different temperatures (250°C and 300°C respectively) are shown in Fig 9 and Fig 10. The presence of a small amount of adsorbed water in both the samples is indicated by the characteristic vibrational mode of O-H stretching and O-H bending. The intensity of these modes in the spectrum of the sample (S2) annealed at a higher temperature is weaker (Fig.10) compared to the sample (S1) annealed at a lower temperature (250°C) (Fig. 9). In the spectrum of nanoparticles of ZnO obtained by annealing the at 250°C, (S1), the characteristic lattice modes of ZnO are observed at 459 cm-1 and 413 cm-1. The positions of these peaks shifted to 436 cm-1 and 420 cm-1 respectively in the spectrum of the sample S2. The XRD results showed that the grain size of the ZnO nanoparticle samples annealed at 300°C is a little larger compared to that annealed at 250°C. Hence the shift of the peaks in the lattice mode region in the spectrum shown in Fig.10 compared to the positions of the corresponding peaks in Fig. 9 can be due to the difference in the grain sizes of the two nanoparticles samples.

Samples	Average grain size (nm)
S1	12.66
S2	14.73
S3	21.40
S4	17.50
S5	23.92

Table 2. Grain size of ZnO nanoparticles synthesized

by varying the pH and annealing temperature of the precursor

Samples	Temp (^{0}C)	pH	Average Grain size (nm)
S4	300	8	17.50
S2		10	14.73
S5	400	8	23.92
S3		10	21.40

Table 3. Comparison of ZnO nanoparticles synthesized at

(a) 300^{0}C and (b) 400^{0}C at two different pH

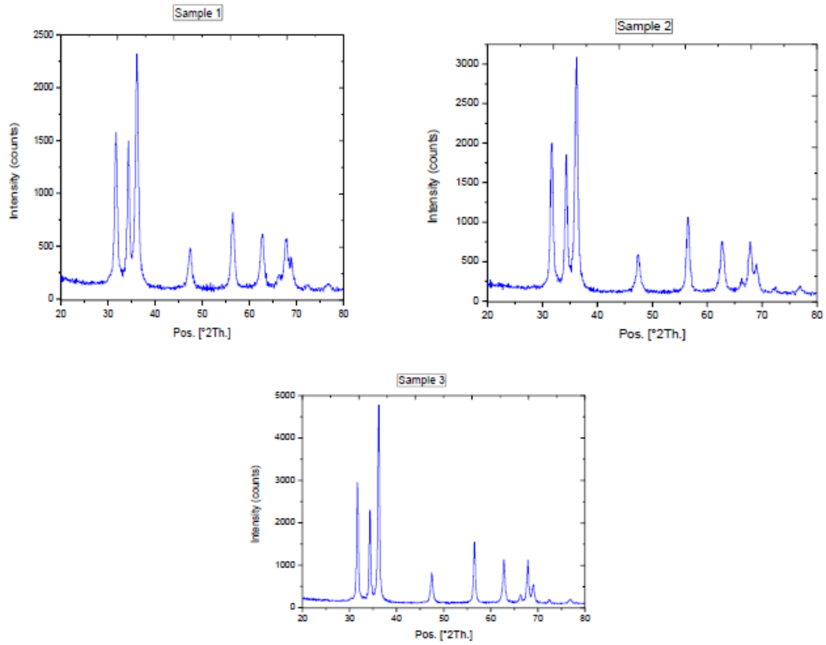

Fig. 2: XRD pattern of ZnO nanoparticles synthesized at pH value of 10 at annealing temperatures (a) 250^{0}C (b) 300^{0}C (c) 400^{0}C

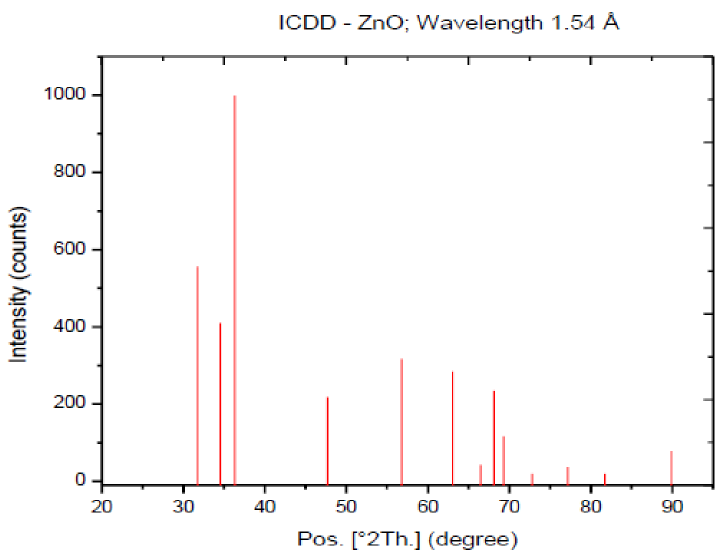

Fig.4: d-spacing of ZnO nanoparticles

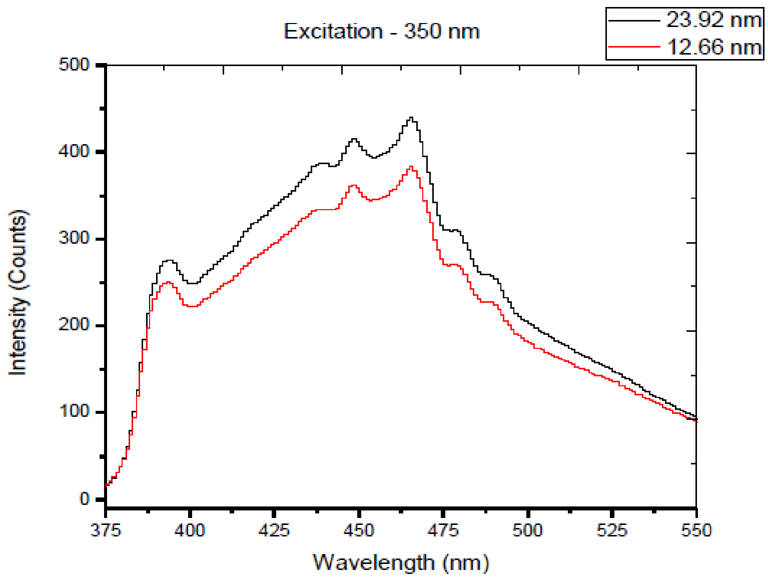

Fig.5: PL of nanoparticles of ZnO at excitation wavelength of 350 nm

Samples	Wavelength of emission (nm)	Intensity (counts)
S1(12.66 nm)	465	386
	448	366
	393	251
S5(23.92 nm)	465	439
	448	414
	393	278

Table.4: Emission wavelength and intensity of ZnO samples (S1 and S5) at 350 nm

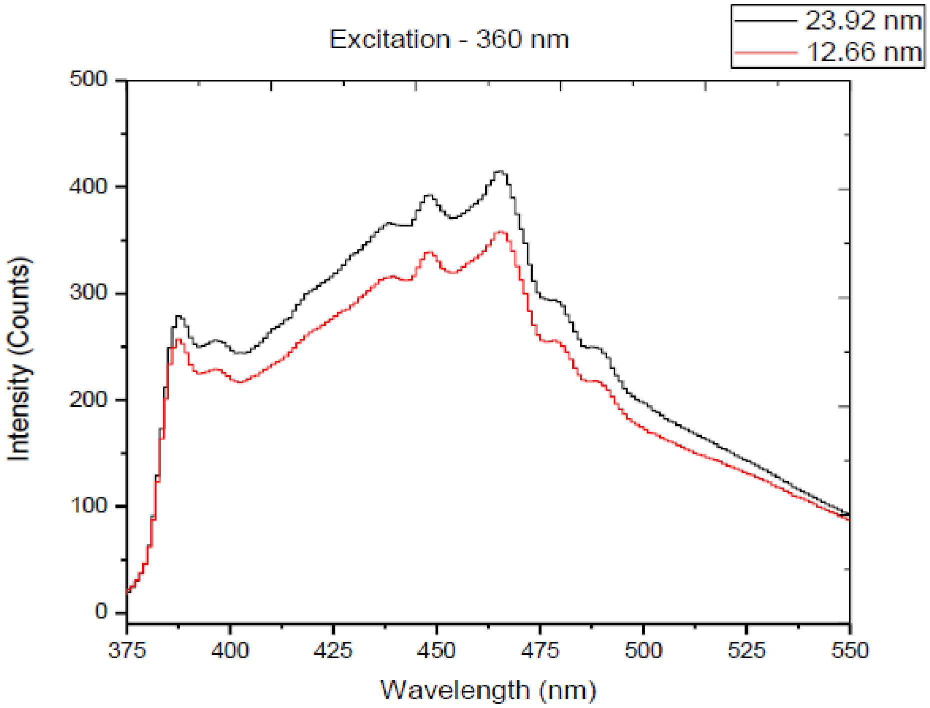

Fig.6: PL of nanoparticles of ZnO at excitation wavelength 360 nm

Samples	Wavelength of emission (nm)	Intensity (counts)
S1(12.66 nm)	465	356
	448	340
	387	253
	360	278
S5(23.92 nm)	465	414
	448	393
	387	278
	360	114

Table 5: Emission wavelength and intensity of ZnO samples (S1 and S5) at excitation wavelength 360 nm

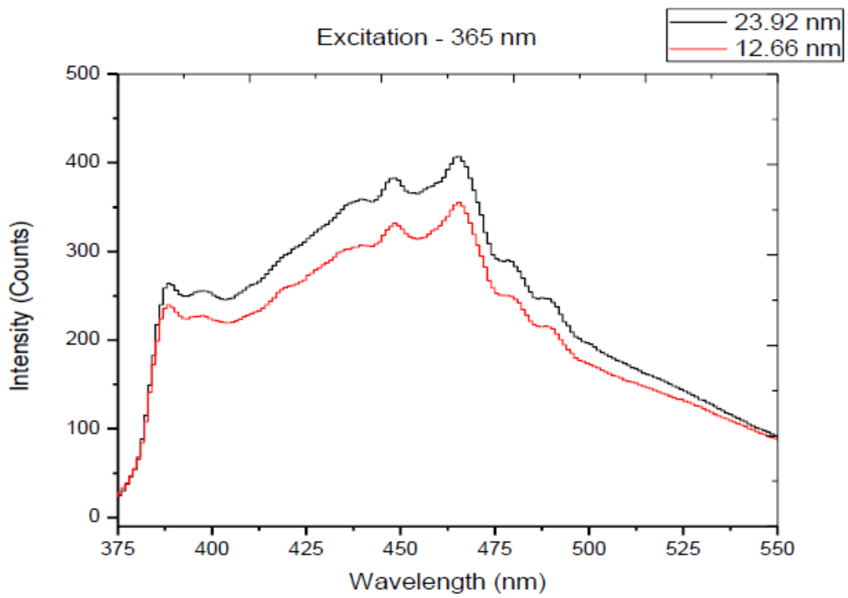

Fig.7. PL of nanoparticles of ZnO at excitation wavelength of 365 nm

Samples	Wavelength of emission (nm)	Intensity (counts)
S1(12.66 nm)	465	343
	448	324
	393	237
	370	High
	740	High
S5(23.92 nm)	465	402
	448	375
	393	267
	370	High
	740	High

Table 6: emission wavelength and intensity of nanoparticles of ZnO (S1 and S5) at excitation wavelength of 365 nm

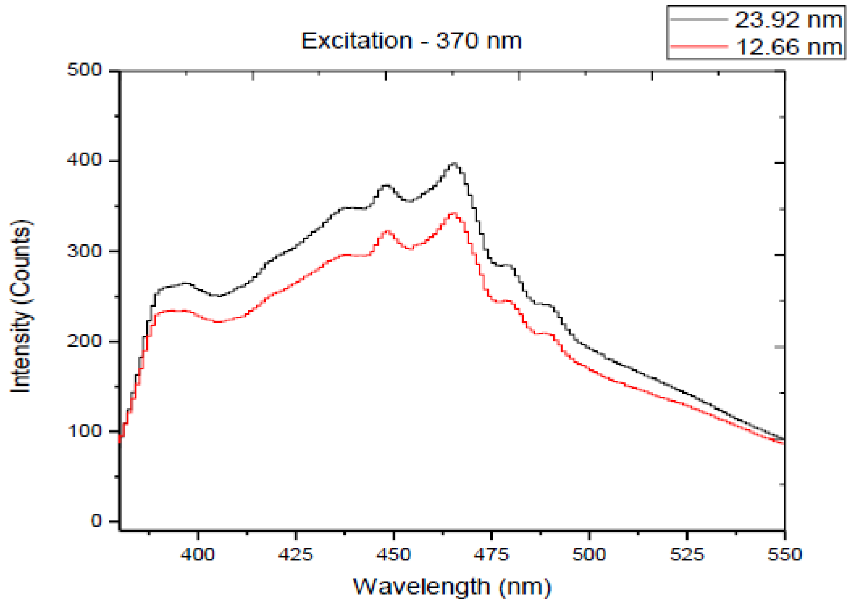

Fig.8. PL of nanoparticles of ZnO at excitation wavelength of 370 nm

Samples	Wavelength of emission (nm)	Intensity (counts)
S1(12.66 nm)	465	343
	448	324
	393	237
	370	High
	740	High
S5(23.92 nm)	465	402
	448	375
	393	267
	370	High
	740	High

Table 7: Emission wavelength and intensity of nanoparticles of ZnO (S1 and S5) at 370 nm

Sample Code	Excitonic peak position (nm)	Average Band gap (eV)
S1 and S5	350	2.84
	360	3.00
	365	2.73
	370	2.84

Table.8. Average bandgap of ZnO samples (S1 and S5) excited at different wavelengths

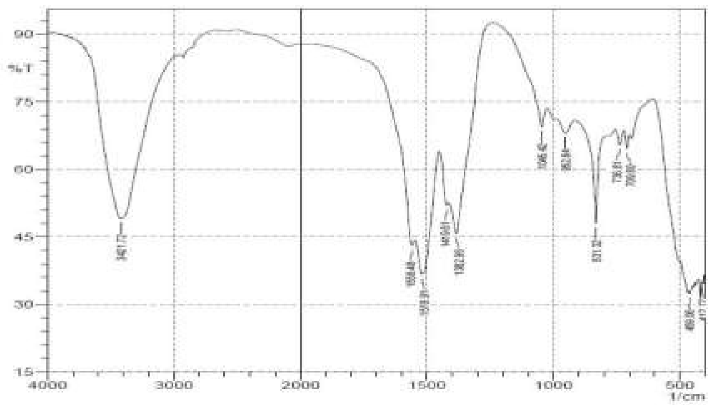

Fig.9. FTIR spectrum of nanoparticles of ZnO synthesized by annealing the precursor at 250°C

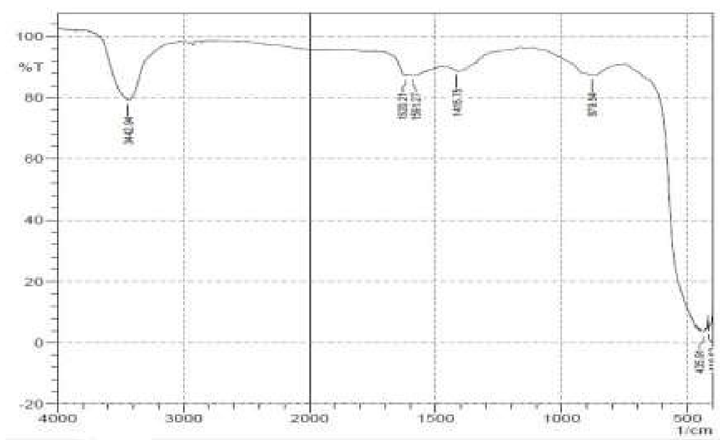

Fig.10. FTIR spectrum of nanoparticles of ZnO synthesized by annealing the precursor at 300°C

Conclusion

Crystalline ZnO with nanometer dimensions are synthesized. The X-Ray diffraction of the samples are taken and the grain sizes are calculated. It was observed that the grain size increases with increase in temperature at constant pH. It is also observed that the grain size decreases with increase in pH at constant temperature. From the detailed X- Ray diffraction study the crystal structure was determined by comparing the Joint Committee on Powder Diffraction Standards (JCPDS)-International Centre for Diffraction Data (ICDD) values. Zinc oxide nanoparticles show Hexagonal (Wurtzite) structure. The photoluminescence spectra of the samples with different grain sizes were compared. The intensity of fluorescent emission of samples with greater grain size was more than the samples with small grain size. There was no shift in the frequency of fluorescence emission for the samples with grain size 12.66 nm and 23.92 nm. This revealed that the effective fluorescent emission of Zinc Oxide lies in the blue region of electromagnetic spectrum. The FTIR spectra of nanoparticles of ZnO were recorded in the range 400-4000 cm-1. It was found that the peaks of ZnO samples associated with O-H vibration mode of adsorbed water molecules, annealed at higher temperature were weaker compared to that annealed at lower temperature.

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