



X-ray Diffraction and Photoluminescence Studies on ZnO Nanoparticles Synthesized by Sol Gel Auto Combustion Method Glycine Assisted Chelating Agent

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Abstract: Zinc oxide (ZnO) nanoparticles were synthesized via a sol gel auto combustion method Glycine assisted chelating agent/fuel. The obtained ZnO nanoparticles were characterized by X-ray powder Diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and photoluminescence spectroscopy technique. The XRD patterns indicate that ZnO nanoparticles was of good crystallinity and having hexagonal wurtzite structure with single phase. The lattice parameter and other structural parameters were calculated from XRD data. The average crystallite size was found 24 nm. FTIR spectra showed the characteristic vibrations frequency band of Zn–O at 453 cm^{-1} . Photo luminescence spectrum showed that two emission peaks at 380 nm and 393 nm, which are ascribed to near band edge transitions. The peak observed at 410 nm is attributed to a violet emission of ZnO nanoparticles. The violet emission at 410 nm is probably due to the defects of zinc interstitial and zinc vacancies related to the interface traps existing at the grain boundaries of ZnO.

Keywords – ZnO, XRD, Photoluminescence, FTIR.

1. INTRODUCTION

Specific attention for Zinc Oxide (ZnO) nanoparticles is always increasing as a result of its wide energy band gap, low toxicity and potential applications for solar cells [1] antibacterial treatments [2], wastewater [3], catalysts photo catalysis [4], food packaging [5]. Basically, ZnO is an n-type semiconductor and II-VI material; its band gap is approximately 3.37 eV, and its excitation binding energy is 60 meV at room temperature and it is a good crystallinity material [6]. It has a hexagonal structure, and the lattice constants are $3.24\text{ Å} - 3.26\text{ Å}$ and $c = 5.13 - 5.43\text{ Å}$. The structural and magnetic properties for ZnO can be properties of ZnO can be enhanced by the partially doping of transition metal ions [7] achieved either by the substitution with different ions or by using different preparation techniques [8, 9]. The magnetic substitution, especially at Co^{2+} , Ni^{2+} ions. Recently, researcher and scientist trying to improve the properties of ZnO with doping of metal ions for different application. Eisenmann Tet al., reported that impact of the transition metal dopant in zinc oxide lithium-ion anodes on the solid electrolyte interphase formation [10]. Ramírez A. E. et al., studied the significantly enhancement of sunlight photocatalytic performance of ZnO by doping with transition metal oxides. His reported results indicate that the introduction of TMO species increase significantly the photocatalytic activity. The sunlight photocatalytic performance in ZnO-doped was greater than bulk-ZnO and in the case of MnO_2 , CoO , Cu_2O and CuO surpasses TiO_2 . This report opens up a new pathway to the design of high-performance materials used in photocatalytic degradation under visible light irradiation [11]. Singh P et al., reviewed the journey of ZnO quantum dots from undoped to rare-earth and transition metal-doped and their applications [12]. Keshari A. K. et al., reported in his research ZnO nanoparticles doping with transition metal elements in polymeric and biomacromolecular matrix and their optical evolution [13]. From his experiment result observed that the transition metal doping and various ligands attached alter the optical and photoluminescence properties. HRTEM results show that the particles are embedded in PVP matrix which leads to stable NPs. XRD and PL results were improved with the use of biotin as surfactant in terms of size and luminescence efficiency. The room temperature ferromagnetism in Fe doped ZnO and its correlation with defects were discussed. Pi M, Zheng L. et al., reported that improved acetone gas sensing performance based on optimization of a transition metal doped WO_3 system at room temperature [14]. Anbuselvan D. et al., studied the room temperature ferromagnetic behavior of nickel-doped zinc oxide dilute magnetic semiconductor for spintronics applications. From experimental result suggest that the band gap measurements showed a red shift from 3.25 to 3.18 eV for the Ni-doped nanoparticles. The vibrating sample magnetometer studies divulge that 3% Ni-doped ZnO

nanoparticles show an intense ferromagnetic property at room temperature. These experimental observations manifested that the Ni-doped ZnO nanoparticles are potential candidates for spintronics device applications [15]. Ranjith Kumar B et al., reported and author adopted A novel green synthesis of the combustion pathway for the preparation of ZnO nanoparticles using Honey and Cow urine. Authors compared with cow urine-prepared ZnO nanoparticles, honey-assisted ZnO nanoparticles demonstrate strong antibacterial activity [16]. Sathish et al., reported that combustion synthesis, characterization and antibacterial properties of pristine ZnO and Ga doped ZnO nanoparticles. From his experimental work, it is found that the undoped and Ga doped ZnO nano powders remarkably enhances the antibacterial activity [17]. Several techniques can be used for synthesizing ZnO nanoparticles such as micro-emulsion [18], sol–gel [19], combustion [20], co-precipitation [21], hydro-thermal [22]. The most efficient technique for preparing ZnO nanoparticles is sol gel auto combustion technique due to its low cost, energy-efficient, easy method and short reaction time. The aim of the present research work was to synthesis ZnO nanoparticles using sol gel auto combustion method and to study their structural and Photoluminescence properties

2. EXPERIMENTAL DETAIL

2.1 Characterization

X-ray diffraction (XRD) analysis of the samples was investigated with a PANalytical X'pert pro diffractometer (Philips PW3373/10) at room temperature. The pattern was recorded using Cu-K α radiation ($\lambda = 1.54182 \text{ \AA}$) in the 2θ range $20^\circ - 80^\circ$ with step size 0.02° and time/step 2 s. Fourier transform infrared spectroscopy (FTIR) of the prepared samples were recorded in the region $4000 - 450 \text{ cm}^{-1}$ on PerkinElmer spectrum -100 spectrophotometer using KBr as a reference material. Photoluminescence properties of ZnO nanoparticles were characterized by F-4500 spectrofluorometer at room temperature. The emission source is a xenon lamp.

2.2. Synthesis of ZnO nanoparticles

Analytical grade chemicals were used for synthesis ZnO nanoparticles. Zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, Sigma-Aldrich 99.999 %), and glycine ($\text{C}_2\text{H}_5\text{NO}_2$, Sigma-Aldrich 99 %), double distilled water (H_2O), (Merck & Co., Inc.) were used. Double distilled water was used as a solvent. Glycine ($\text{C}_2\text{H}_5\text{NO}_2$) was used as a chelating agent i.e., as a fuel. The fuel ratio was taken according to stoichiometric proportion of metal nitrate to oxidizer ratio (1:1) [23]. In a typical synthesis of ZnO nanoparticles, the appropriate proportion of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and $\text{C}_2\text{H}_5\text{NO}_2$ were completely dissolved in a minimum amount of double distilled water to get the aqueous solution. The aqueous solution was then stirred for about 1 h in order to mix the solution uniformly. The mixed solution was evaporated to dryness by heating at 120°C on a hot plate with continuous constant stirring and finally formed a very viscous gel. The viscous gel was ignited by increasing temperature up to 200°C and the loose and burnt powder of the samples was obtained. Finally, the burnt powder was sintered at 700°C for 4 h to obtain zinc oxide nanoparticles. The resulting powders white in colour. The samples were ground for a half an hour and used for XRD and FTIR and PL characterization

3. RESULTS AND DISCUSSIONS

3.1 X-ray diffraction study

The X-ray diffraction patterns of ZnO nanoparticles are shown in Fig. 1. From the X-ray diffraction pattern analysis it is observed that all the diffraction peaks in the XRD pattern well match with the standard pattern of pure ZnO (JCPDS: 36- 1451) [24]. From the analysis of XRD pattern of ZnO nanoparticles revealed the formation of hexagonal wurtzite structure.

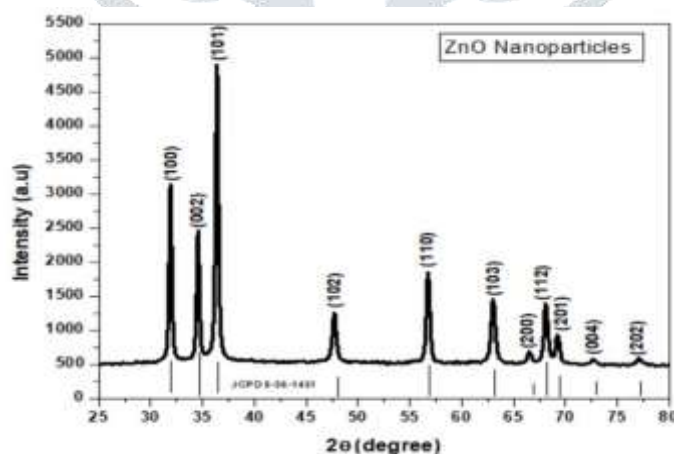


Fig.1 X-ray diffraction pattern for ZnO nanoparticles.

The lattice parameters (a and c), crystal sizes (t) unit cell volume (V), the dislocation density (D) and the Zn–O bond length (L) of zinc oxide determined by using [25]. All the structural parameter are given in table 1. All the structural data of synthesized ZnO nanoparticles is in reported range [25].

Table. 1. Lattice parameters ('a' and 'c'), c/a ratio, crystallite size (D), positional parameter (u) and bond length (L), Volume of unit cell (V), X-ray density (ρ_x), and atomic packing fraction (APF) of ZnO nanoparticles.

Parameter	Lattice parameters		c/a	D (nm)	(u)	(L) Å	V (Å) ³	ρ_x (gm/cm ³)	(APF) %
Value	a = 3.2467 (Å)	c = 5.2076 (Å)	1.6002	24.00	0.3801	1.9814	47.811	5.6352	75.38

3.2 Fourier transform infrared Spectroscopy (FTIR)

In order to confirm the formation of ZnO nanoparticles fourier transform infrared measurement technique was used. The characteristic peaks exhibited by FTIR spectra of ZnO nanoparticles is shown in Fig. 2.

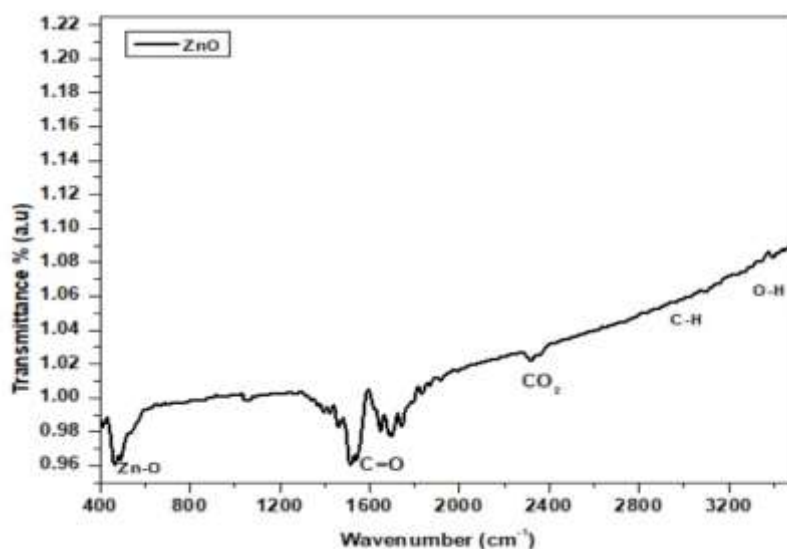


Fig. 2 FTIR spectra of ZnO nanoparticles

The two absorption peaks are observed between 1656 and 1400 cm^{-1} corresponding to asymmetric and symmetric stretching of the carboxyl group (C=O) [26]. The broad absorption peaks show the presence of O–H stretching mode of H_2O in the ZnO nanocrystals around 3387 cm^{-1} for ZnO sample [27]. The absorption peaks observed between 2355 cm^{-1} is because of the existence of O–C–O molecule in the atmosphere. The main absorption band of Zn–O stretching, vibration at 453 cm^{-1} for ZnO samples [28]. From the FTIR study, it is confirmed that the formation of ZnO nanoparticles synthesized by sol gel auto combustion technique.

3.3. Photoluminescence Spectroscopy (PL)

Room temperature photoluminescence (PL) emission spectra of ZnO nanoparticles is shown in Fig. 3. ZnO on its own luminesces in the visible and UV regions. In the visible region the emission is attributed to intrinsic defects induced during the synthesis itself. The UV emission is due to excitonic recombination.

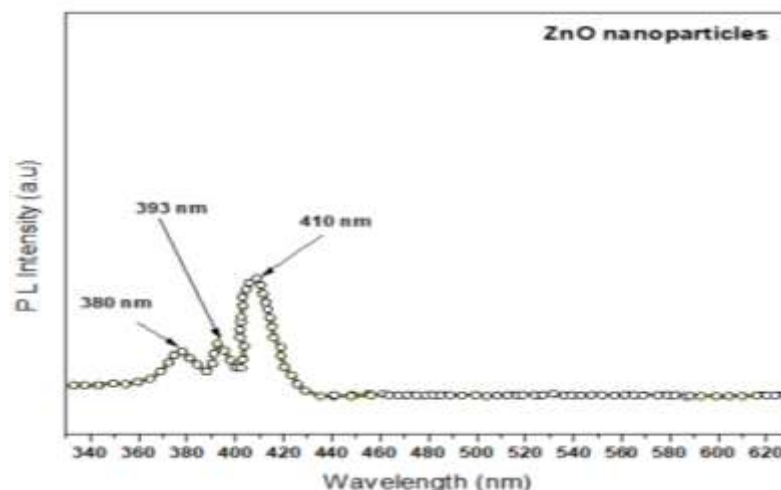


Fig.3. Photoluminescence (PL) emission spectra of ZnO nanoparticles at room temperature

Various luminescence emissions in the visible region are possible depending upon the synthesis procedure, morphology, vacancies, and surface defects. From the synthesized ZnO nanoparticles photoluminescence spectra, UV emission peaks of lowest wavelength are observed at 380 nm and 393 nm, which correspond to the nearest band emission (NBE) of ZnO[29]. The peak observed at 410

nm is attributed to a violet emission of ZnO nanoparticles. The violet emission at 410 nm is probably due to the defects of zinc interstitial (Zn_i) and zinc vacancies (V_{Zn}) related to the interface traps existing at the grain boundaries of ZnO[30].

4. CONCLUSIONS

ZnO nanoparticles have been successfully synthesized by sol–gel auto combustion method by using of glycine as a chelating agent. The single-phase nature of the ZnO was confirmed from X-ray diffraction data. The particle size was calculated from the most intense peak (101) using Scherrer formula and is in the range of 24 nm. The structural data of the present ZnO nanoparticles is in the reported range. Photoluminescence spectrum shows two emission peaks, at 380 nm and 393 nm, which correspond to the nearest band emission (NBE) of ZnO. The peak observed at 410 nm is attributed to a violet emission of ZnO nanoparticles. The violet emission at 410 nm is probably due to the defects of zinc interstitial and zinc vacancies related to the interface traps existing at the grain boundaries of ZnO.

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