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# Influence of precursors on morphology and spectroscopic properties of ZnO Nanoparticles

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## Abstract

ZnO Nanopowders are prepared with three different precursor's viz., NaOH, KOH and Na<sub>2</sub>CO<sub>3</sub> using co-precipitation method. Further samples are characterized by X-ray diffraction (XRD), Scanning electron microscopy (SEM), UV-Vis Optical absorption and Photoluminescence (PL) spectroscopy analyses. Morphology and optical properties of ZnO nanoparticles are investigated for the each precursor. XRD patterns indicate hexagonal phase unit cell structure. ZnO nanoparticles exhibit an absorption band at 355 nm and two photoluminescence bands peaking at 397 nm & 530 nm. From the analyses of results, it is very clear that precursors used in the present study have played a vital role in surface morphology, structural and optical properties of ZnO nanoparticles.

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**Keywords:** ZnO Nanopowder, UV-vis absorption, FT-IR, Photoluminescence

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## 1. Introduction

Semiconducting materials have attracted a wide attention due to their unique properties and immense potential application in various Opto-electronic device fabrications. Specifically, low-dimensional semiconductor

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nanostructures have been of great interest due to their size dependent properties viz., scaling of the energy gap and corresponding change in the optical properties. Out of all semiconducting materials, Zinc oxide (ZnO) is a distinctive electronic and photonic wurtzite n-type semiconductor with a wide direct band gap of 3.37 eV, high exciton binding energy (60 meV) at room temperature and high melting temperature 2248 K [1, 2]. In ZnO, oxygen and zinc atoms are spatially arranged in a way that O atoms are arranged in a closed hexagonal structure, while the Zn atoms occupy the centre of the distorted tetrahedron structure. The high exciton binding energy of ZnO is a predominant feature that makes it suitable for laser emission due to high radiative recombination efficiency for spontaneous emission as well as a lower threshold voltage. Lot of attention has been paid towards ZnO nanoparticles as they exhibit unique properties viz., high chemical stability, and low dielectric constant, good photoelectric and piezoelectric activities [1-3]. ZnO nanoparticles are considered to be promising candidates for various technical applications, such as nanogenerators, gas sensors, biosensors, solar cells, varistors, photo detectors, and photo catalysts [4-7].

## 2. Experimental Methods

### 2.1. Materials

Zinc chloride ( $\text{ZnCl}_2$ ), sodium hydroxide (NaOH), potassium hydroxide (KOH), sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) and Ethanol ( $\text{C}_2\text{H}_6\text{O}$ ) were purchased and used without further purification.

### 2.2. Synthesis of Zinc Oxide Nanoparticles

Zinc oxide nanoparticles were synthesized by wet chemical method using zinc chloride, NaOH, KOH and  $\text{Na}_2\text{CO}_3$  precursors. In this experiment, a 0.4 M aqueous ethanol solution of zinc chloride ( $\text{ZnCl}_2$ ) was kept under constant stirring using magnetic stirrer to completely dissolve the zinc nitrate for one hour and 0.8 M aqueous ethanol solution of sodium hydroxide (NaOH) was also prepared in the similar way with stirring of one and half hours. After complete dissolution of zinc chloride, 0.8 M NaOH aqueous solution was added under high speed constant stirring, drop by drop (slowly for 50 min) touching the walls of the vessel. The reaction was allowed to proceed for 2 hrs after complete addition of sodium hydroxide. The dripping of the  $\text{ZnCl}_2$  and NaOH solutions in an aqueous alkaline solution results in immediate precipitation of ZnO, and the color of the suspension changes from transparent to white. The beaker was sealed at this condition for 2 h. After the completion of reaction, the solution was allowed to settle for overnight and further, the supernatant solution was detached carefully. The remaining solution was centrifuged for 10 min and the precipitate was removed. Thus precipitated ZnO nanoparticles were cleaned three times with deionized water and ethanol to remove the by-products which were bound with the nanoparticles and then dried in a vacuum oven at a maximum temperature of 70°C for several hours. During drying,  $\text{ZnCl}_2$  is completely converted in to ZnO. In a similar manner, ZnO nanoparticles were synthesized from zinc chloride with different precursors potassium hydroxide and sodium carbonate. Further, three samples of ZnO nanoparticles were characterized by for their optical and nano-structural properties using X-ray diffraction, scanning electron microscopy, UV-Vis absorption and Photoluminescence spectra.

The labeling for the ZnO nano powders prepared with three different precursors is shown below.

NZ: ZnO nanopowder with NaOH

KZ: ZnO nano powder with KOH

CZ: ZnO nano powder with  $\text{Na}_2\text{CO}_3$

### 2.3. ZnO Nanoparticle Characterization

#### 2.3.1. X-Ray Diffraction (XRD)

X-ray diffraction patterns for the ZnO nanoparticles were recorded using an X-ray diffractometer (PANLYTICAL) using secondary monochromatic  $\text{CuK}_\alpha$  radiation of wavelength  $\lambda = 0.1541$  nm at 40 Kv/50mA in the scan range  $2\theta = 20$  to  $90^\circ$ . Samples were supported on a glass slide.

#### 2.3.2. Scanning Electron Microscopy (SEM)

Morphology of the samples was investigated using scanning electron microscope (SEM with EDXA, Sirion) which also has been used for compositional analysis of the prepared ZnO nanoparticles. A drop of nanoparticles dissolved in methanol was placed on a copper grid.

#### 2.3.3. UV-Visible Absorption Spectra

The optical absorption spectra of ZnO nanoparticles were recorded using a UV-VIS spectrophotometer (Hitachi, U-3010). The particles were dissolved in methanol, and solution was placed in a quartz cuvettes with 1 cm path length.

#### 2.3.4. Photoluminescence (PL) Spectra

The photoluminescence (PL) spectrum of the ZnO nanoparticles dissolved in methanol has been measured using a spectrofluorometer (F-2500 FL Spectrophotometer, Hitachi).

## 3. Results and Discussion

### 3.1. X-ray Diffraction

ZnO structures with different grain sizes can be obtained by using different precursors. Fig. 1 represents the X-ray diffraction patterns of ZnO nano particles prepared with three precursors. From the patterns it is evident that a definite line broadening of the XRD peaks indicate nano level range of particles in the the prepared material. From XRD patterns analyses, we determined peak intensity, position and width, full-width at half-maximum (FWHM) data. The diffraction peaks located at  $31.84^\circ$ ,  $34.52^\circ$ ,  $36.33^\circ$ ,  $47.63^\circ$ ,  $56.71^\circ$ ,  $62.96^\circ$ ,  $68.13^\circ$  and  $69.18^\circ$  have been keenly indexed as hexagonal wurtzite phase of ZnO [8] with lattice constants  $a=b= 0.324$  nm and  $c= 0.521$  nm (JPCDS card no: 36-1451) [9] and further it also confirms the synthesized nano powder was free of impurities as it does not contain any characteristic XRD peaks other than ZnO peaks. The average ZnO nanoparticle diameter was calculated using Debye-Scherrer formula [10]

$$d = \frac{0.89\lambda}{\beta \cos\theta} \quad (1)$$

where 0.89 is Scherrer's constant,  $\lambda$  is the wavelength of X-rays,  $\theta$  is the Bragg diffraction angle and  $\beta$  is the full width at half-maximum (FWHM) of the diffraction peak corresponding to plane  $\langle 101 \rangle$ . From all diffraction patterns, it is very clear that the plane (101) is found to be more intense than other peaks. More intensity of the plane (101) indicates the direction of crystal growth along the c axis (direction [0001]) of the ZnO wurtzite structure. The average particle size of the sample was found to be 16.21 nm which is derived from the FWHM of more intense peak corresponding to 101 plane located at  $36.33^\circ$  using Scherrer's formula. From the patterns, it can be concluded that all the peaks match very well with the standard wurtzite structure [9] and the FWHM of high intense (101) diffraction peak increases with the usage of precursors in the order NaOH, KOH and  $\text{Na}_2\text{CO}_3$ . It might be due to the fact that the molar ratios of  $\text{OH}^-$  to  $\text{Zn}^{2+}$  in the case of NaOH & KOH and  $\text{CO}_3^{2-}$  to  $\text{Zn}^{2+}$  in the case of  $\text{Na}_2\text{CO}_3$  are the key factors in forming ZnO nanoparticles.

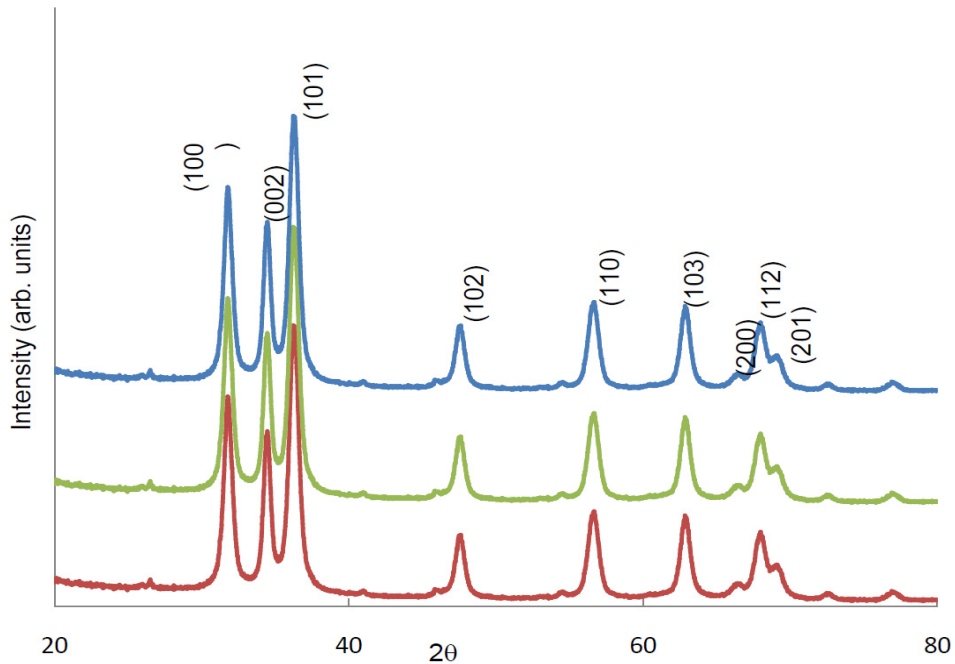


Fig.1. Comparison of XRD Pattern of ZnO nanoparticles with Different Precursors

### 3.2 .SEM Pictures

The morphology and size of the synthesized ZnO particles are studied by scanning electron microscopy (SEM). Fig. 2 represents the SEM pictures of prepared ZnO nano particles at different magnifications. These pictures confirm the formation of ZnO nanoparticles. SEM micrographs of ZnO nano powders with three precursors exhibit (Figure 2) particles of nano meter size and particles found to have an irregular spherical shape along with narrow particle size distribution. It is also observed that most of the particles exhibit some faceting. The estimated particle size from SEM pictures found to be varying between 10 and 40 nm for all the samples. The lower particle size with different morphology shows that precursors along with same solvent are playing a key role in controlling the nucleation and crystal orientation. From the pictures, it also can be seen that the size of the nano particle is less than 20 nm which was in good agreement with the particle sizes (18.2 nm) calculated from the above mentioned Debye-Scherrer formula.

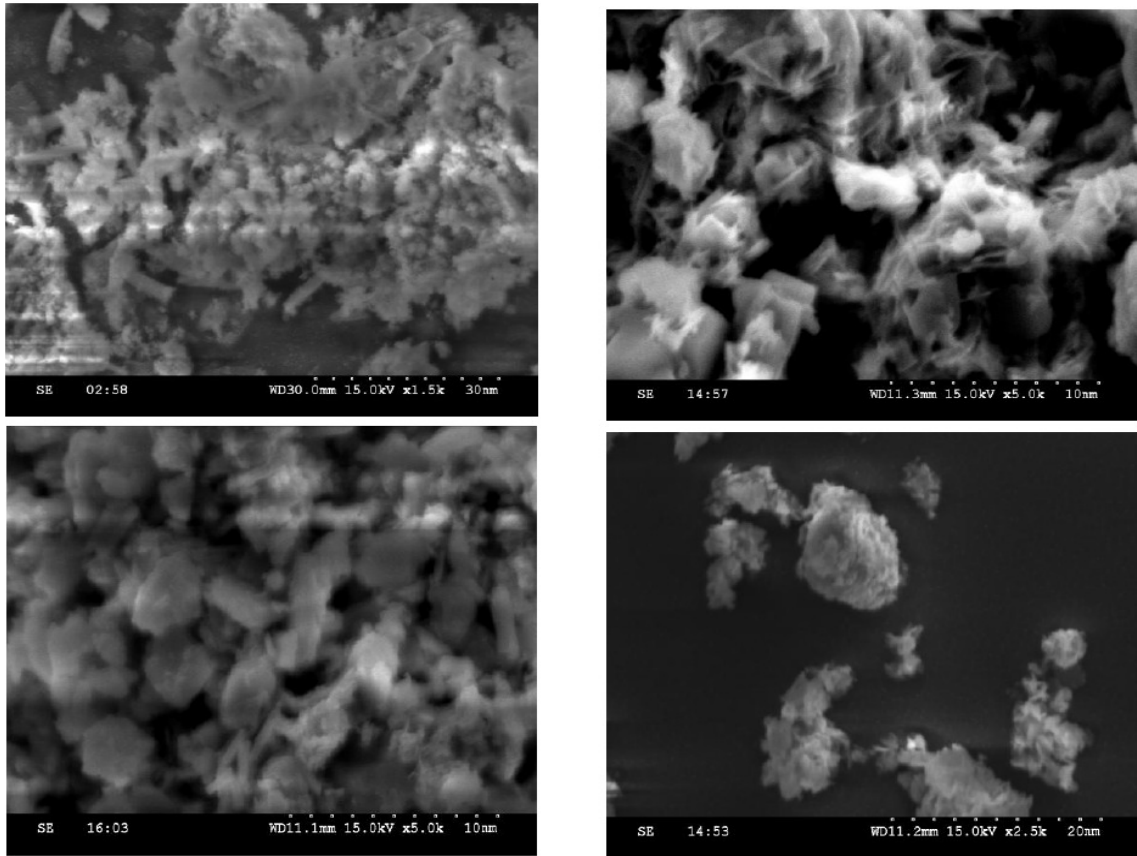


Fig.2.SEM pictures of ZnO Nanoparticles synthesized with various precursors at different magnifications

### 3.3 .UV-Vis absorption Spectra

The UV-Vis absorbance spectra of ZnO nano powder with different solvents are shown in Figure 3. From the spectra, it is very clear that all of them exhibit strong absorption band with maxima around 345-360 nm (~3.54 eV) and another excitonic absorption band located in the range 260-267 nm. It is quite interesting that band gap corresponding to strong absorption band is wider than that of bulk ZnO, which has a band gap of 3.37 eV (corresponding to 368 nm). The exciton absorbance band is attributed to the effect of quantum confinement for small nanocrystals [11, 12]. The spectra also confirm mono-dispersed nature for nano particle distribution as spectra exhibit significant sharp absorption of ZnO [11, 12]. It can be seen from the spectra that precursors used do not have any considerable impact on the position of strong absorption band so that size of the particle. But there is very small shift in the absorbance maximum with the use of precursors in order NaOH, KOH and Na<sub>2</sub>CO<sub>3</sub>, the shift might be associated with the broader nanoparticle distribution such that broader exciton absorbance.

The average particle size in a nanocolloid can be calculated from the absorption onset from UV-Vis absorption spectra by using effective mass model [13, 14] where the band gap  $E^*$  can be approximated by

$$E^* = E_g^{bulk} + \frac{\hbar^2 \pi^2}{2er^2} h \left( \frac{1}{m_e^* m_0} + \frac{1}{m_h^* m_0} \right) - \frac{1.8e}{4\pi\epsilon\epsilon_0 r} - \frac{0.124e}{\hbar^2 (4\pi\epsilon\epsilon_0)^2} \left( \frac{1}{m_e^* m_0} + \frac{1}{m_h^* m_0} \right)^{-1} \quad (2)$$

where  $E_g^{\text{bulk}}$  is the bulk band gap expressed in eV,  $\hbar$  is Plank's constant,  $r$  is the particle radius,  $m_e$  is the electron effective mass,  $m_h$  is the hole effective mass,  $m_0$  is free electron mass,  $e$  is the charge on the electron,  $\epsilon$  is the relative permittivity, and  $\epsilon_0$  is the permittivity of free space. Due to the relatively small effective masses for ZnO ( $m_e = 0.26$ ,  $m_h = 0.59$ ), band gap enlargement is expected for particle radii less than about 3.7 nm [13]. The following equation was derived from the effective mass model given above with small mathematical simplification [14] which is used to find the size of the particle from the absorbance spectra,

$$r(\text{nm}) = \frac{-0.3049 + \sqrt{-26.23012 + \frac{10240.72}{\lambda_p(\text{nm})}}}{-6.3829 + \frac{2483.2}{\lambda_p(\text{nm})}} \quad (3)$$

where  $\lambda_p$  is peak absorbance wavelength in nm. The size of ZnO nanoparticles for three different precursors in order NaOH, KOH and  $\text{Na}_2\text{CO}_3$  are calculated from their corresponding excitonic absorbance peaks. The sizes of particles found to be more or less same with an average size of 3.1 nm. These results are verified and confirmed by the SEM pictures presented above.

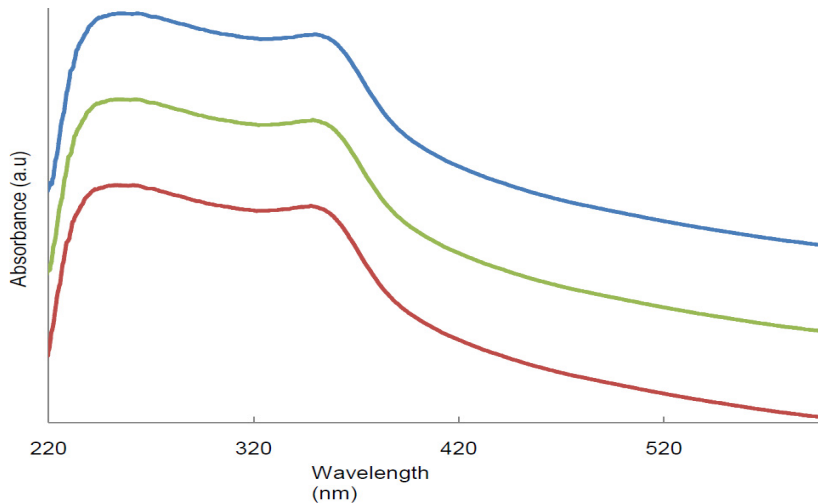


Fig. 3. UV-vis Absorption spectra of synthesized ZnO nanoparticles

### 3.4 .Photoluminescence Spectra

The photoluminescence originates from the recombination of surface states. The strong photoluminescence indicates that the surface states remain very shallow, as quantum yields of band edge will decrease exponentially with increasing depth of surface state energy levels [12, 15, 16]. The photoluminescence spectra of all three samples are shown in Fig. 4. The spectra have been recorded at room temperature under excitation wavelength 320 nm. As presented in previous papers, the spectra exhibit two emission peaks, one is located at around 392 nm (uv region) corresponds to the near band gap excitonic emission [17] and the other is located at around 520 nm. This is trap-state emission that results from radiative decay of excited electrons from surface states to the ground state. The highest intensities in trap-state emissions are observed for nanocrystals obtained in the presence of  $\text{Na}_2\text{CO}_3$  [18, 12]. As observed in UV-visible absorption spectra, there is no significant change in the position of both the emission peaks. Due to broader distribution of nanoparticles in NaOH, the intensity and full-width at half-maximum (FWHM)

are found to be small in comparison with the ZnO nano particles in the presence of KOH and  $\text{Na}_2\text{CO}_3$ . Furthermore, the spectra also support the narrow size distribution of nano particles in the powder due to narrow peak [19].

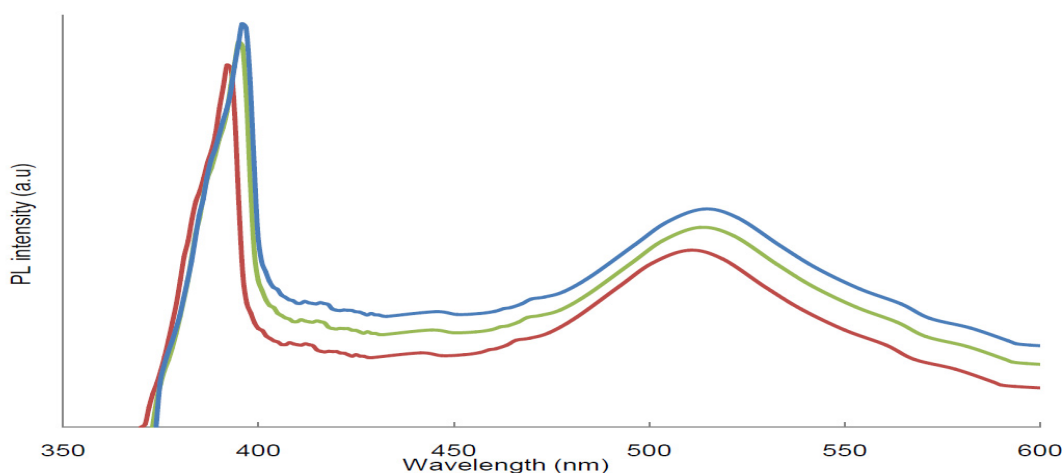


Fig. 4. PL spectra of synthesized ZnO nanoparticles excited with 320nm

## Conclusions

In this paper, we have reported the synthesis of ZnO nanoparticles in the presence of NaOH, KOH and  $\text{Na}_2\text{CO}_3$  using co-precipitation method. Later samples are characterized by XRD, SEM, UV-vis absorption and photoluminescence spectroscopy. XRD and SEM studies confirmed the nanostructures for the prepared ZnO nanoparticles. UV-Vis absorption spectra exhibit two bands one at around 345 to 360 nm and another in the range 258 to 265 nm. All the samples exhibit bands in the same range but samples with NaOH found to exhibit broader distribution among all. From these spectra, average particle size also calculated and verified from SEM pictures. The calculated average particle size of the prepared ZnO nano powder found to be 18.2 nm for peak absorbance wavelength. Photoluminescence spectra recorded at room temperature under  $\lambda_{\text{exc}} = 340$  nm exhibit sharp UV band corresponds to near band gap excitonic emission and broad green emission band due to the oxygen vacancy. The sample with  $\text{Na}_2\text{CO}_3$  exhibit better PL intensity out of all samples due to narrower distribution of nano particles.

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