*J. Mater. Environ. Sci. 7 (1) (2016) 331-336*
*ISSN : 2028-2508*
*CODEN: JMESCN*

# Structural characterization and surface environment of ZnO nanoflowers

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*Received 02 Mar 2015, Revised 16 Oct 2015, Accepted 18 Oct 2015*

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**Abstract**

In this paper, ZnO nanoflower was successfully obtained by precipitation method using zinc nitrate and sodium hydroxide at pH 11.5. The aggregate sturucture evolutions were characterized by XRD, SEM, and FESEM while the elemental composition of the materials was determined by EDX. The petals of the nanoflower are of varying sizes. The crystalline size of the nanoparticles is in the range 39.5-53.1 nm and the calculated surface area has been found to be 27.1 g/m$^2$. Infrared study reveals that the nano crystals are not homogeneous and the chemical structural environment has shown hydroxide layer attached on the surface of the ZnO nanoparticles. This work has provided some knowledge on the structural and surface properties of ZnO nanomaterials.

*Keywords*: Nano flower, nanocrystalline material, surface hydroxyl group

## 1. Introduction

Considerable interest has been focussed by various workers on the surface and structural properties of ZnO nanoparticles who provided some supporting evidence to understand the overall nature of the nanomaterials [1-5]. Various workers have reported different synthetic methods and applications of the nanomaterials [6-13]. Strictly speaking, the surface properties are to some extent related with the structural morphologies of ZnO nanomaterials, e.g. nanorods, nanowires, nanoflowers, nanotubes, etc., synthesised by varying methods [14]; however, the surface environment of the material, compositional, and structural aspects of the nanoparticles, when prepared in aqueous solution, promise to explore some unprecedentate information ..

Zinc oxide is described as hexagonal wurtzite structure where $Zn^{2+}$ and $O^{2-}$ ions form an ionic bond. Since coordination number of the ions is four each, this suggests that each $Zn^{2+}$ ion is tetrahedrally surrounded by four $O^{2-}$ ions and vice versa. Again, a regular tetrahedron is equally compatible with purely ionic interaction and with covalent bonding involving sp$^3$ hybrid orbitals [15]. If the lattice coordination number is four or less, there is possibility of the formation of the covalent linkages in the crystal [16].

The Zn-O bond possesses ionic character and thus it lies on the borderline between being classified as a covalent or ionic compound with an iconicity of $f_i$ = 0.616 on the Phillips iconicity scale [17]. Moreover, electronegativity of zinc is enough (1.65) to serve as an electron acceptor, but the electronegativity of oxygen is more (3.44) than that of zinc. According to Pauling, when the electronegativity difference between two elements is 1.7, the bond formed by these elements is 50% ionic and 50% covalent [18]. In the case of ZnO, the difference of electronegativity is 1.79. Both ionic and covalent bond character of ZnO molecule is distinctly evident because it is known that pure ionic bonding does not occur even in cases where there are large electronegativity difference [19]. It is true because it has been reported that ZnO is a polar molecule and has polar covalent bond [14].

The nature ZnO nanomaterials require some further explanation. Moreover, the surface property of nanomaterials is prepared by precipitation method in not largely known. The precipitation method is generally done at quite high pH, therefore, association of single and/double electrical layer of some species [20] is quite logical on the surface of the nanoparticles. However, the literature on the chemistry of the adsorbed species on ZnO surface is very few in number. Therefore, surface and structural characterization of ZnO nanoparticles call for an in-depth study.

We give here a compilation of data in order to examine various aspects of the ZnO nanoparticles, prepared by precipitation method at an alkaline pH.

## 2. Materials and methods

### *2.1. Preparation of ZnO nanoparticles*

Zinc oxide nanoparticles were prepared by t precipitation method. 150 ml aqueous solutions of 0.45M $Zn(NO_3)_2.6H_2O$ and 0.9M NaOH as precursors and soluble starch (0.1%) as stabilizing agent were prepared. The alkali solution was added drop wise to the zinc nitrate solution with constant stirring with an electric stirrer at a speed of 1000 rpm. The reaction was allowed to proceed till the pH of the solution attained 11.0. After attaining the constant pH 11.5, the solution was kept overnight (20 hours) at room temperature ($28^oC$). The supernatant solution was discarded and the remaining part was centrifuged out followed by washing with ethanol. The solid material was dried in air. It was further heated in an oven at 70 $^oC$ for two hours. The dried white material is ZnO nanoparticles.

### *2.2. Instrumental analysis*

The crystalline nature of the synthesized ZnO nano material was verified by X-Ray Diffraction (XRD) pattern. The XRD measurements of the particles was carried out using a Bruker AXS and the X-ray diffraction was determined with CuKα radiation with wavelength, $\lambda = 1.54178A^o$ at the Bragg angle (2 theta) ranging from $10 – 100^o$ at a scan rate of 50 $min^{-1}$. The Scanning Electron Microscope (SEM) analysis was carried out using LEO 1430 VP Scanning Electron Microscope coupled with Oxford EDX system (INCA X-ray microanalysis). Infrared spectrum was recorded in KBr pellet by using a Perkin-Elmer IR spectroscopy in the range 4000-400 $cm^{-1}$.

## 3. Results and discussion

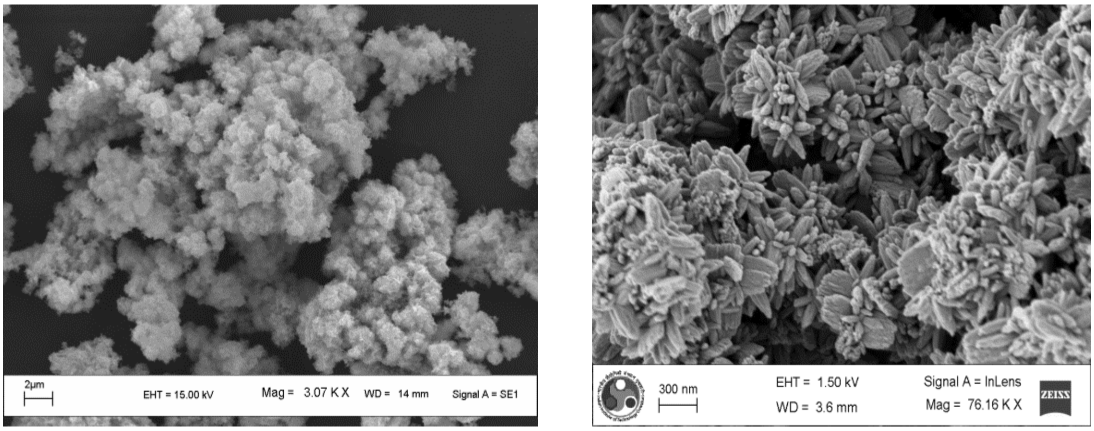
### *3.1. SEM and FESEM*

We have examined the surface morphology of ZnO nanoparticles by scanning electron microscope (SEM) and field emission scanning electron microscope (FESEM). The images show that there is formation of distinct three dimensional ZnO nanoflowers with microstructure aggregates, the petals of the nanoflower are of varying sizes (Figure 1). The more or less dense layer of nanoflowers is not homogeneous, showing the underlying layer composed of nanorods/nanowires, leading to nanotexturation.

### *3.2. XRD*

Charaterisation of the nanoparticles by X-ray diffraction (XRD) has shown diffraction pattern in the 2θ range from $10\text{-}100^o$ (Figure 2). All the diffraction peaks are well matched with the Joint Committee on Powder Diffraction Standards (JCPDS-36-1451) for bulk ZnO. Nevertheless the results provide valuable information. The lattice parameters of ZnO are:

A = 0.3249 nm and c = 0.5206 nm. The ratio c/a has been reported to be 1.633 for an ideal hexagonal closed packed structure. Our result of c/a ratio is 1.6023 which is almost close to the ideal value (1.633) of hexagonal cell. The major reflections between $30^o$ and $40^o$ (2θ values) indicate more crystallinity regions of the nanoparticles. Less intense peaks at $47.6^o$, $56.7^o$, $63^o$, $68^o$ and $69^o$ (2θ values) also reveals crystallinity. Further, the peaks have high intensity and narrower spectral width, thus strongly suggesting good crystallinity of the nanomaterials.



(a) (b)

Figure1. (a) SEM and (b) FESEM images of ZnO nanoparticles

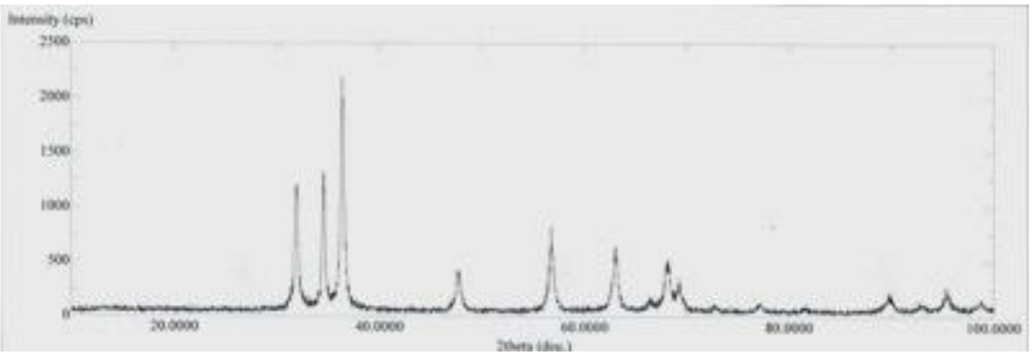


Figure 2. XRD spectrum of ZnO nanoparticles

The crystallite size of the synthesised ZnO nanoparticles has been calculated using Debye-Scherrer equation [21]. The observed diffraction peak of high relative intensity for ZnO , is used to calculate the crystallite size and found to be 39.5 nm. The crystallite sizes of the particles are lying between 39.5-53.1 nm. Moreover, the calculated surface area [22] of the nanomaterials has been found to be 27.1 g/m$^2$.

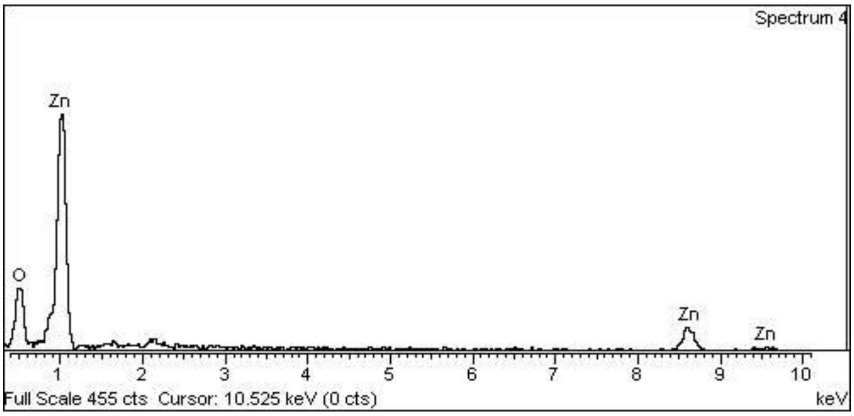
### *3.3. EDX*

Coupled to SEM, EDX spectroscopy gives an important quantitative information regarding elemental composition of the nano particles. The EDX spectrum, given in figure 3, has shown three distinct peaks for zinc atom and that one peak for oxygen atom. As there appears no peak for other elements, this strongly suggests high purity of the synthesized ZnO nanomaterials. The weight percentage determined by EDX spectroscopy for zinc and oxygen atoms do not account for 1:1 ratio of the elements.

### *3.4. IR*

In order to understand the nature of bondings occurring in the ZnO naomaterials, prepared here, infrared study seems to be good enough to permit identification of them. IR bands for single crystal of ZnO occurred for two fundamental modes of vibration- one parallel and the other perpendicular to their six fold axes. For parallel modes, the bands occur at 377 and 578 cm$^{-1}$ and for the perpendicular mode, the bands appear at 406 and 589 cm$^{-1}$ [23]. The bands in the lower region (377 and 406 cm$^{-1}$) and relatively in the higher region (575 and 589 cm$^{-1}$)

for these two modes of vibration do not differ much. Again, in the powder form of ZnO, IR bands are reported to occur at 440, 493 and 530 cm$^{-1}$ [23].



| Element | Weight% | Atomic% |
|---|---|---|
| O K | 24.35 | 56.80 |
| Zn L | 75.65 | 43.20 |
| Totals | 100.00 | |

**Figure 3.** EDX spectrum of ZnO nanoparticles and elemental analysis

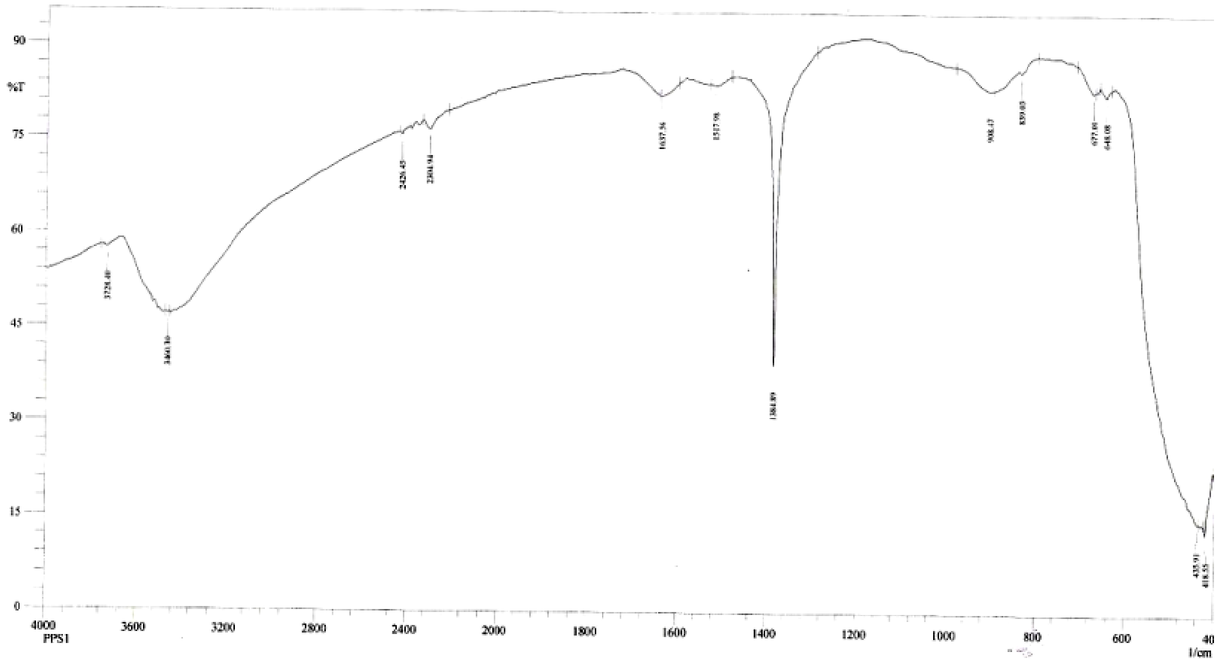


**Figure 4.** IR spectrum of ZnO nanoparticles

In the IR spectrum, shown in figure 4, the bands appeared at 418 and 435 cm$^{-1}$ in the region of 400-600 cm$^{-1}$. The bands reported to occur in the range of 500-600 cm$^{-1}$ for single crystal and powder forms of ZnO, are absent in the spectrum. The bands at 418 and 435 cm$^{-1}$ are not strong enough and may be attributed to perfect crystal lattice and also to powder form where association of other molecules or non-stoichiometry of the molecules. One point of agreement between the reported band at 406 cm$^{-1}$ for perpendicular mode of single crystal of ZnO and our result (band at 418 cm$^{-1}$) could be attributed crystalline form of the nanoparticles. Again, the band at 440 cm$^{-1}$ for powder form of ZnO almost agrees well with the band at 435cm$^{-1}$, observed in this study. These reveal that there is insignificant distinction between the bands in both the cases. As regards to such observations, it is worthwhile to emphasize that the nanomaterials prepared for this study are not all homogeneous.

It is now possible to know the surface bondings other than Zn-O bond of the nanomaterials which are associated with the crystal. A broad IR band of medium intensity is observed in the region of 3400-3500 cm$^{-1}$ of the spectrum (Figure 4). The band at 3460 cm$^{-1}$ can be attributed to O-H stretching vibration; the presence of hydrogen bonding cannot be ruled out. Our finding is similar to that of Jong-hun et al [24] who reported a band at 3438 cm$^{-1}$ for O-H stretching vibration in the ZnO nanomaterials prepared by different methods. Further evidence of the presence of hydroxyl group is the occurrence of a sharp band with high intensity at 1384 cm$^{-1}$ (Figure 4). This band can be assigned to O-H in-plane bending vibration. This is possible because the in-plane bending vibration of the hydroxyl group generally observed in the region of 1330-1420 cm$^{-1}$ [25]. On the basis of the IR data, it is further supported that there is occurrence of hydroxo, oxo and/or aquo species on the surface and thereby strongly provide an unprecedented result of excess oxygen content in the nanomaterials, synthesised for this study. Further, the presence of excess oxygen content, as recorded by the EDX spectroscopy, finally proofs of the formation of such complexes and their retention in the nanoparticles.

The synthesis of nanoparticles by the precipitation method (in aqueous solution) is predominantly pH dependant. Degen and Kosee [20] while studying the effect of pH on the surface charge of ZnO in aqueous solution reported hydroxide layer or negative charged surface at high pH. Moreover, the surface charge can originate from the presence of oxo ion [26]. Within this context, we have studied the surface charge on the particles. We believe that at pH 11.5 hydroxyl ions are largely available in the aqueous solution and when both oxide and hydroxide of zinc are produced (initially in colloidal form [27]), these ions would be adsorbed on the surface of colloidal materials. To maintain the electrical neutrality, the surface charges on the particles are compensated by an array of opposite charge which are secondarily adsorbed (as $Zn^{2+}$ and/or $Zn(OH)^+$ [20]) ; thus forming an electrical double layer. On heating, there would be thermal motions of the particles and the adsorbed species could scarly permit rigid array of charge on the surface which is supported that ZnO preparations have hydroxyl groups on the surface [4] but this can be removed by heating [3]. Consequently, gradual depletion of the electrical double layer is possible. In our study, the materials were heated up to 80°C, there would be quite possibility of formation of perfect crystal of ZnO; however, presence of hydroxo, oxo and/or aquo species in the complex of zinc ion are quite logical, as the formation of hydroxo complex has been known [3]. Further, the depletion of electrical double layer could be true because the polar surface of ZnO is highly metastable in nature and is responsible for several unique and astonishing properties including piezoelectric properties [18].

In the precipitation method in aqueous solution, the formation of such complexes containing hydroxo, oxo and/or aquo ligands can be easily explained in the light of coordination chemistry. These are suitable ligands which can donate one electron pair to the metal ion. Again zinc ion has empty 4s- and 4p- orbitals and thus involvement of $sp^3$ hybridisation is quite possible. Therefore, the coordinate covalent bond formation is justified because in each case, the four coordination number of $Zn^{2+}$ ion is maintained. Further the superimposition of these components finally makes the entire structure of ZnO extremely stable. Now, it is proper to mention that the synthesised ZnO nanoparticles have crystal structure with intermediate ionic-covalent bonding rather than discrete molecular structure.

## Conclusion

This study has shown the systhesis of 3-D ZnO nano flower by the precipitation method. It is not practicable to show here the exact OH groups attached with ZnO crystal surface but EDX and IR studies have substantially proved the excess oxygen content and O-H bonding, respectively. Attempts to visualise the bonding assemblage, $sp^3$ hybridisation, and structural properties of the nanomaterials have been successful. An investigation is in progress to determine magnetic property and structural behaviour of mixed oxides containing ZnO in order to gather advanced knowledge for the synthesised ZnO nanoparticles.

**Acknowledgement-**The authors are grateful to Dr L Baruah, Principal, NNS College, Titabar for providing facilities to carry out this work and to the Directors, IIT, Guwahati and CSIR-NEIST, Jorhat for instrumental analysis. MKB is thankful to UGC-NERO for the financial support under MRP scheme (F.5-27/2013-14/MRP/NERO).

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