

***In situ* precipitation and characterization of nano zinc oxide in different polymeric media and photoluminescent properties**

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Abstract

Zinc oxide (ZnO) nanoparticles were prepared using zinc chloride and ammonium hydroxide with proper concentration in different polymeric mediums by in situ precipitation method. The polymeric mediums used were chitosan, starch and polyvinylalcohol (PVA). The structural properties of the synthesized ZnO nanoparticles have been confirmed using the Scanning Electron Micrographs. The crystallinity and particle size of the nano particles were also determined.

From the surface morphology, it is clear that the prepared ZnO is nano in nature and the shape of ZnO changes with respect to the medium of precipitation. The ZnO particles obtained from chitosan medium exhibit cuboidal shape while those obtained from starch have cylindrical shape and coral shape from PVA medium. Photoluminescence studies of the sample with three different media were also studied.

Keywords: Nano ZnO, Chitosan, Starch, PVA, Luminescence.

Introduction

Nanoparticles of metal oxides have become extremely popular in technical and industrial areas of studies. This is on account of the changes in their optical, electrical, magnetic and catalytic properties like thermal stability mechanical hardness, or chemical passivity^{13,14,19}. Many physical properties of nanoparticles differ significantly from single crystals with the same chemical composition. When crystallites reach the nanoscale size, they are affected by the quantum confinement effect of the electronic states and the existence of a large number of surface atoms which affects the properties of nanomaterials in comparison to their bulk phases.

Nano crystalline oxide particles have technological applications; they are used as catalysts^{5,6,31}, passive electronic components and high performance ceramics. Nano structured materials are used in pharmaceuticals, biomaterials, catalysts and supports, membranes and filters, paint pigments, cosmetics, medical diagnostics, batteries and fuel cells, electronics, magnetic and optical devices, structured materials and protective coatings^{2,16,20}. Zinc oxide has electromechanical, semi-conductivity and piezoelectric properties. It is a functional oxide that exhibits near

fluorescent emission. The nano-central symmetry gives piezoelectric property to ZnO and this property is exploited in making transducers and sensors. ZnO nanomaterials provide excellent prospects for photonics and nanoelectronics. A wide array of nano structures like nano rods, nano belts, nano rings etc. can be designed by ZnO.

These properties made ZnO, the material of the 21st century as per the report by Materials Today²³ due to its relevance in both basic research and practical applications like solar energy conversion, luminescence, photo-catalysis, electrostatic dissipative coating, transparent UV protection films, chemical sensors and varistors.

Various techniques are used for preparing ZnO nanoparticles such as, sol–gel technique¹⁵, microemulsion synthesis²¹, mechanochemical processing²³ by thermal decomposition of organic precursor, spray pyrolysis, RF plasma synthesis, supercritical-water processing²⁴, vapour transport process, self-assembling, sonochemical or microwave-assisted synthesis, direct precipitation²⁵, homogeneous precipitation¹⁰, chemical co-precipitation²⁶, chemical vapour deposition, thermal decomposition¹, hydrothermal synthesis¹², solid-state reaction, spray pyrolysis²² and microemulsion precipitation. Precipitation technique, one of these synthetic ways, offers a simple means for low cost and large-scale manufacturing that does not require costly raw materials and costly equipment in contrast to other traditional methods.

Numerous studies have concentrated on the analysis of variables impacting the characteristics of stable zinc oxide nanoparticles in order to overcome the difficulties²⁹. The pH of the reaction mixture, the temperatures for synthesis and calcination, the length of the reaction, the concentrations of the precursors, the solvent medium and the concentration of the surfactant are some of these variables⁴. The factors mentioned earlier like the particle size, morphology, phase and surface area directly influence the nanoparticles of the zinc oxide^{4,9,18}.

The unique characteristics of zinc oxide make it one of the most important nano materials in future research and applications. The diversity of nano structures of ZnO will open up many new fields of research in nanotechnology as the properties strongly depend on the dimensions and morphologies^{7,27}. In the present study, an *in situ* preparation of nano ZnO was done in different polymeric media like chitosan, starch and polyvinylalcohol (PVA). A comparative

study of ZnO obtained from various media was done by Scanning electron microscopy (SEM), X-ray diffraction studies (XRD) and particle size analyzer. A comparison of the luminescence properties was also studied.

Material and Methods

Analytical grade solvents and chemicals were used throughout. ZnCl_2 , commercial nano Zinc Oxide, NH_4OH starch and polyvinyl alcohol were all products of Merck. Chitosan was obtained from India Sea Foods, Kannammali, Kochi. The XRD data were recorded on Xpert PRO MPD. The scanning electron microscope studies were performed on an equipment with model number JSM-7600 F. Analysis of particle size was performed on a Microtrac .

Preparation of ZnO: *In situ* precipitation method was used to prepare zinc oxide. The precipitation medium was prepared using 2% polymer solution. The flow chart depicts schematic overview of zinc oxide preparation. Dissolve 2g

chitosan in 100 ml of 2% acetic acid and stir it with the help of a magnetic stirrer for 1-2 hr. Add 5gm of ZnCl_2 slowly by stirring continued for 1 hour. Then added 12 ml of NH_4OH drop by drop with stirring. After half an hour stirring, the solution is kept undisturbed for 12 hours. The resulting precipitate was filtered and repeatedly washed with distilled water and the precipitated $\text{Zn}(\text{OH})_2$ was dried and calcined at 400°C .

The same procedure is followed in the preparation of ZnO by using starch and polyvinyl alcohol medium

Results and Discussion

Zinc Oxide has been prepared using *in situ* precipitation method. Different polymeric media like chitosan, starch and PVA were used for precipitation. The precipitated $\text{Zn}(\text{OH})_2$ was dried and calcined at 400°C . Characterization of samples prepared was done using XRD, SEM and particle size analyzer.

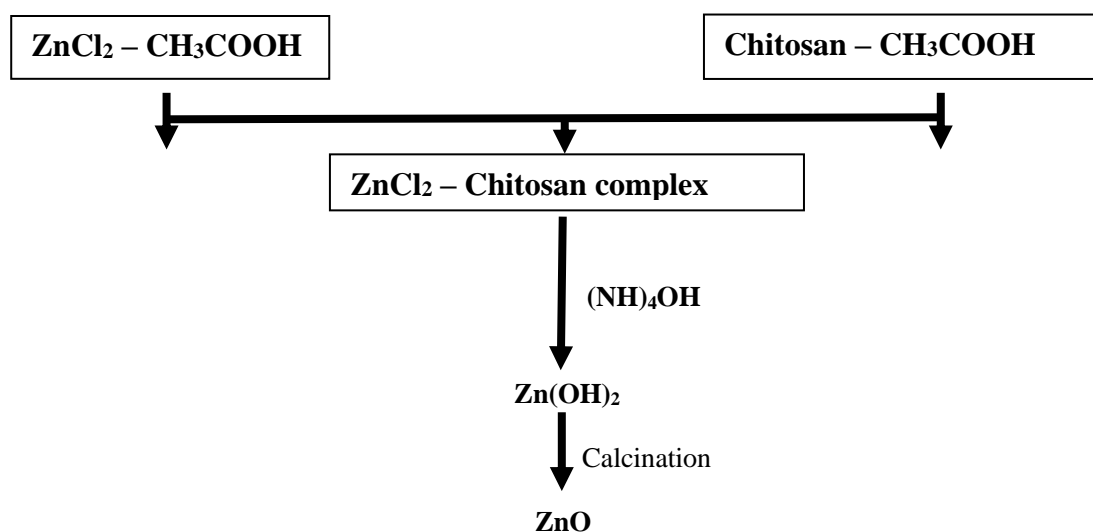


Figure 1: Schematic representation of *in situ* preparation of ZnO in chitosan medium

Sample 1

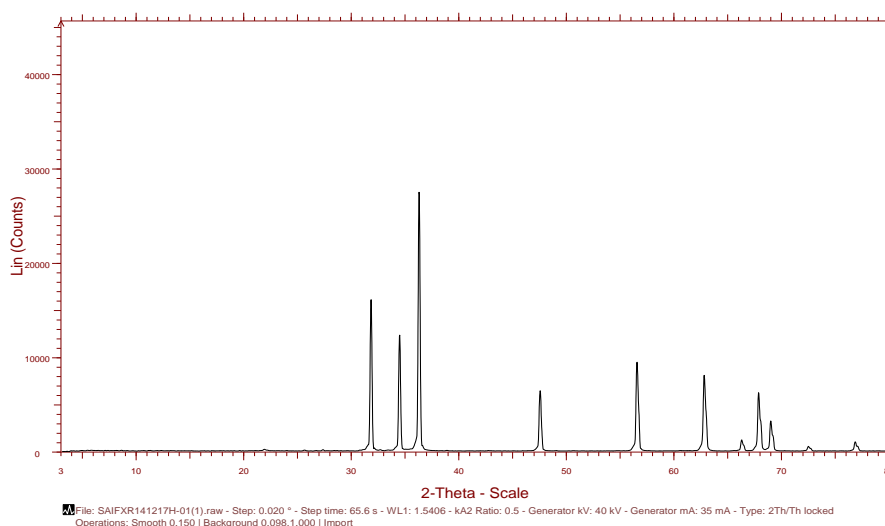


Figure 2: XRD pattern of ZnO in chitosan medium

X-RAY diffraction studies (XRD): ZnO prepared from chitosan medium shows that the highest peak is observed at 36.278° with full width half maximum FWHM value as “.202”. Figure 2 shows the RD pattern of ZnO in chitosan medium.

Figure 3 shows the XRD pattern of ZnO prepared by using starch medium. The XRD pattern of zinc oxide in starch shows the similar pattern as that of zinc oxide in chitosan. The chitosan and starch are natural biopolymer giving the similar XRD patterns of metal oxide as precipitated from it. The highest peak is observed at 36.186° and with FWHM value as “.203”. There is a difference between the metal oxides prepared from these two polymeric media.

ZnO is also prepared by using synthetic polymer PVA. Figure 4 shows the XRD pattern of ZnO precipitated in PVA. The XRD pattern of ZnO in PVA shows maximum peak at 35.939° and the FWHM value as “.260”. The full width half maximum value of ZnO from this medium is slightly greater than that of other two media.

Scanning electron microscope (SEM) studies: Surface morphology of the prepared ZnO was characterized using SEM. The scanning electron micrographs of ZnO prepared in chitosan medium (Fig. 5) show that the particles have a cylindrical cuboidal structure and with non uniform crystallites.

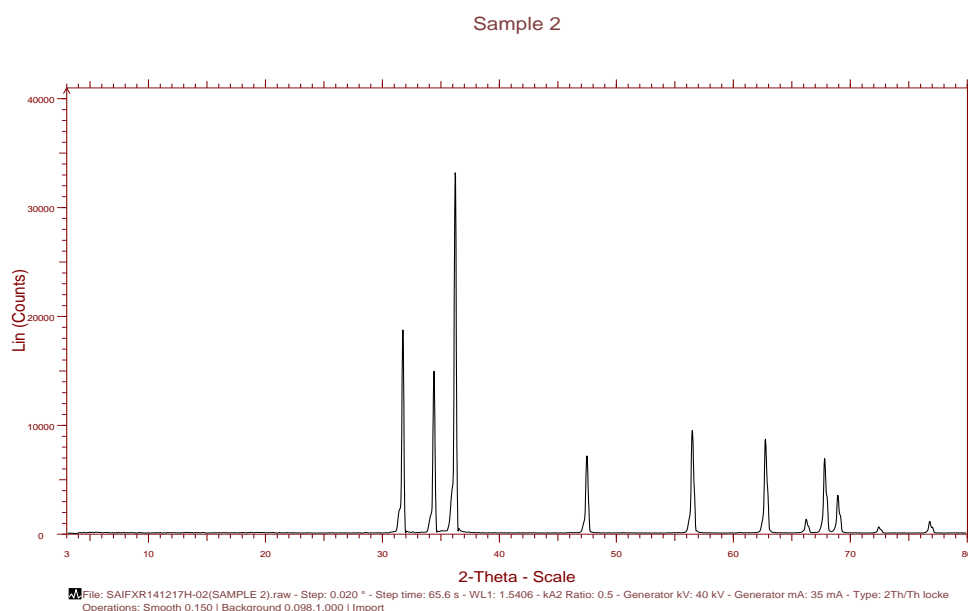


Figure 3: The XRD pattern of ZnO in starch medium

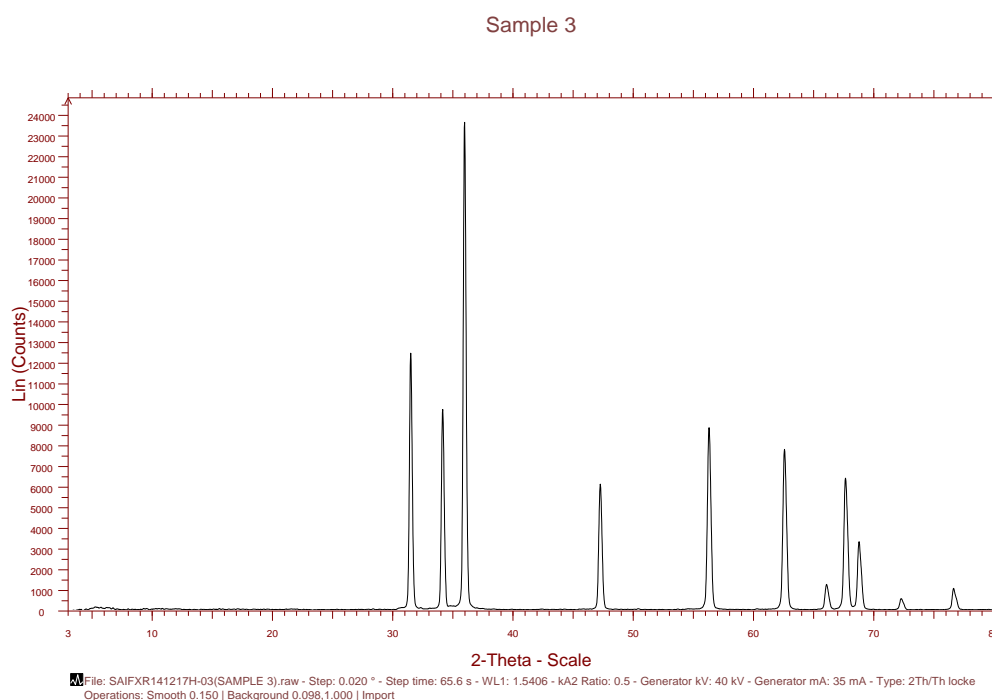


Figure 4: The XRD pattern of ZnO in PVA

The scanning electron micrographs of ZnO prepared from starch medium are shown in fig. 6. It is clear from the figure that the zinc oxide formed is crystalline and has got cylindrical structure.

The scanning electron micrographs of ZnO prepared from PVA is shown in fig. 7. Zinc oxide formed has a coral shape and the crystals formed show uniformity.

For comparative study we have also taken the SEM photograph of commercial nano ZnO (Fig. 8). It has been observed that commercial nano ZnO shows a honey comb structure.

Thus it is clear that there is variation in shape as well as in size with respect to the medium of preparation. The difference in shape of crystals may be due to the difference in the formation of metal-polymer complex. The structure of the complex changes with polymer medium and that results in the difference in morphology of ZnO crystals.

Particle size analysis

Comparison of Particle Size: The grain size of zinc oxide prepared from zinc chloride in different media like chitosan, starch, PVA was determined and compared (Table 1). The crystal size of each zinc oxide sample and the entire width at half maximum of a hkl peak at theta value demonstrate that zinc oxide prepared from PVA has smaller crystal size than zinc oxide prepared from other mediums. Additionally, it has been noted that zinc oxide made from chitosan exhibits a high particle size but a low FWHM value.

Natural polymer media like chitosan and starch gave almost same crystallite shape and size. But low molecular weight PVA gave smaller particle size and coral shape. All these depend on the structure of metal-polymer complex. Compared to chitosan and starch, PVA has low molecular weight and good water solubility, these two parameters enhance the stability of the complex formed. The formation of smaller crystallites of ZnO depends on the stability of the complex and diffusion of the reacting species.

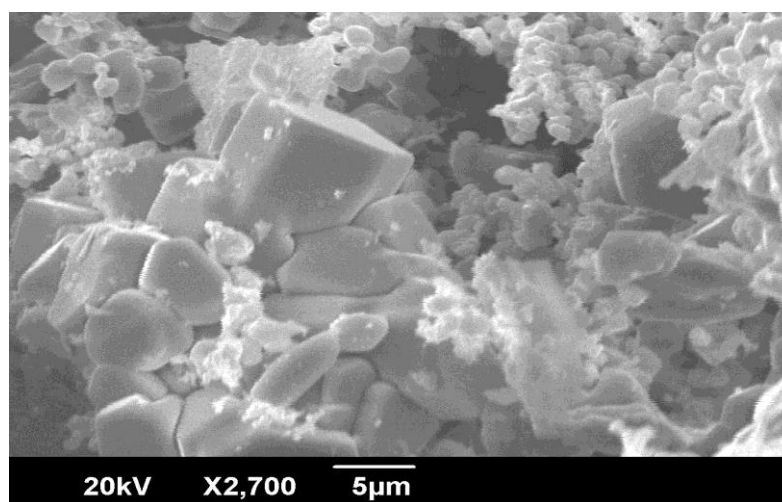


Figure 5: SEM Micrograph of nano ZnO in Chitosan

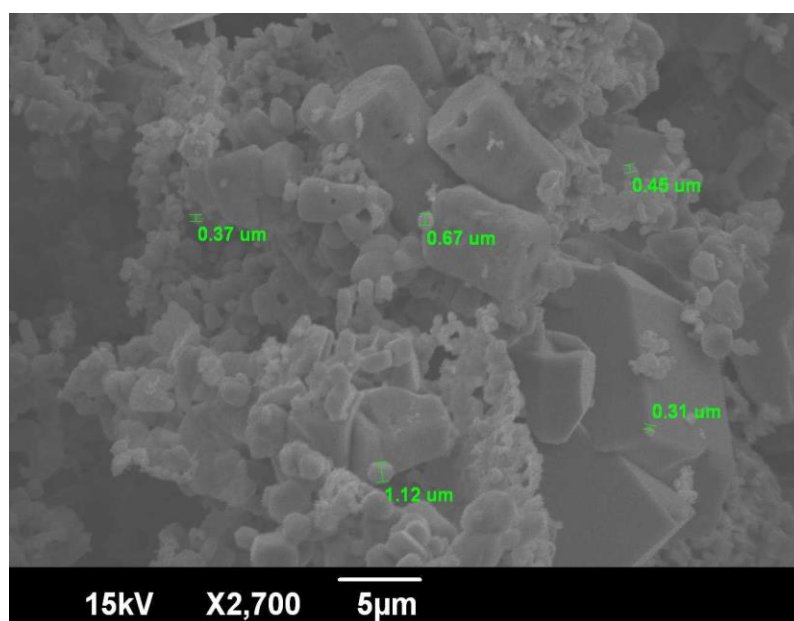


Figure 6: SEM Micrograph of nano ZnO in Starch

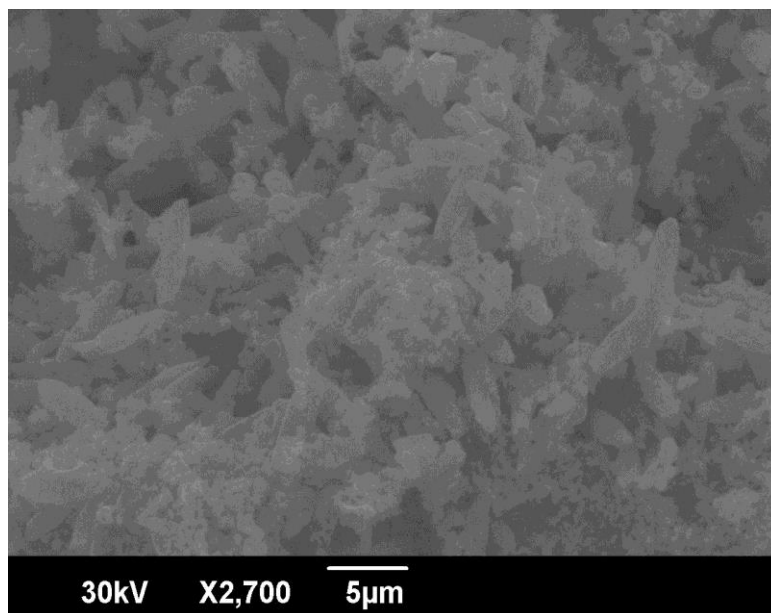


Figure 7: SEM Micrograph of nano ZnO in PVA

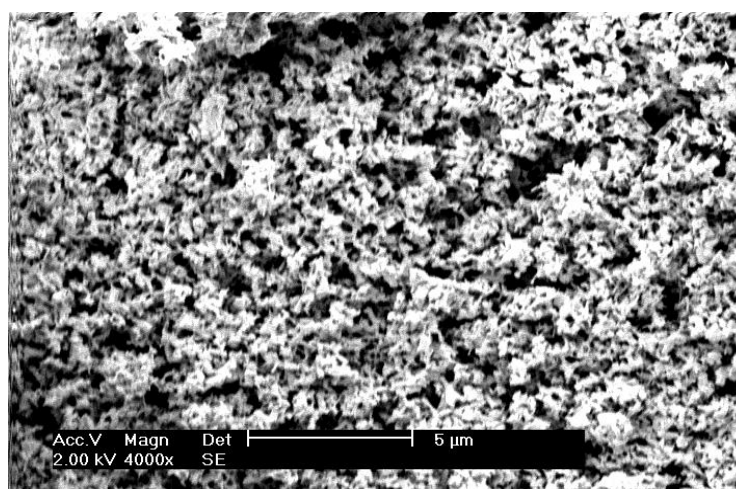


Figure 8: SEM Photograph of amorphous commercial zinc oxide

Table 1
Comparison of Particle size

ZnO Sample	FWHM Value	Crystallite Size (nm)
ZnO/CHITOSAN	0.202	5.7724
ZnO/STARCH	0.203	5.7372
ZnO/PVA	0.260	4.4654

Comparison of luminescent properties:

Photoluminescence study of the sample prepared was carried out and is shown in figures 9 a, b and c. It has been found that nano ZnO prepared in three different media shows green luminescence. Zinc oxide in Chitosan shows the green luminescence at 600 nm whereas ZnO prepared in starch and PVA mediums shows green luminescence at 500 nm.

The luminescence properties of ZnO prepared in Starch and PVA mediums are in agreement with the fluorescent properties of ZnO nanostructures fabricated by hydrothermal method done by Zhiwei et al³⁰. They recorded the fluorescence spectra of nanostructures created on a Zn

substrate with various reactant solution of pH values stimulated at 327 nm. It is clear that the nanostructure created was of ZnO because of the strong peak at the edge of the ultraviolet area, which is consistent with ZnO's band-edge emission.

Typically, flaws introduced during the fabrication process are what generate the broad peak at roughly 500 nm in the fluorescence spectra of the ZnO in starch and PVA⁸. This peak appears weakly in the fluorescence spectrum, suggesting that the manufactured ZnO has decent optical characteristics under this condition.

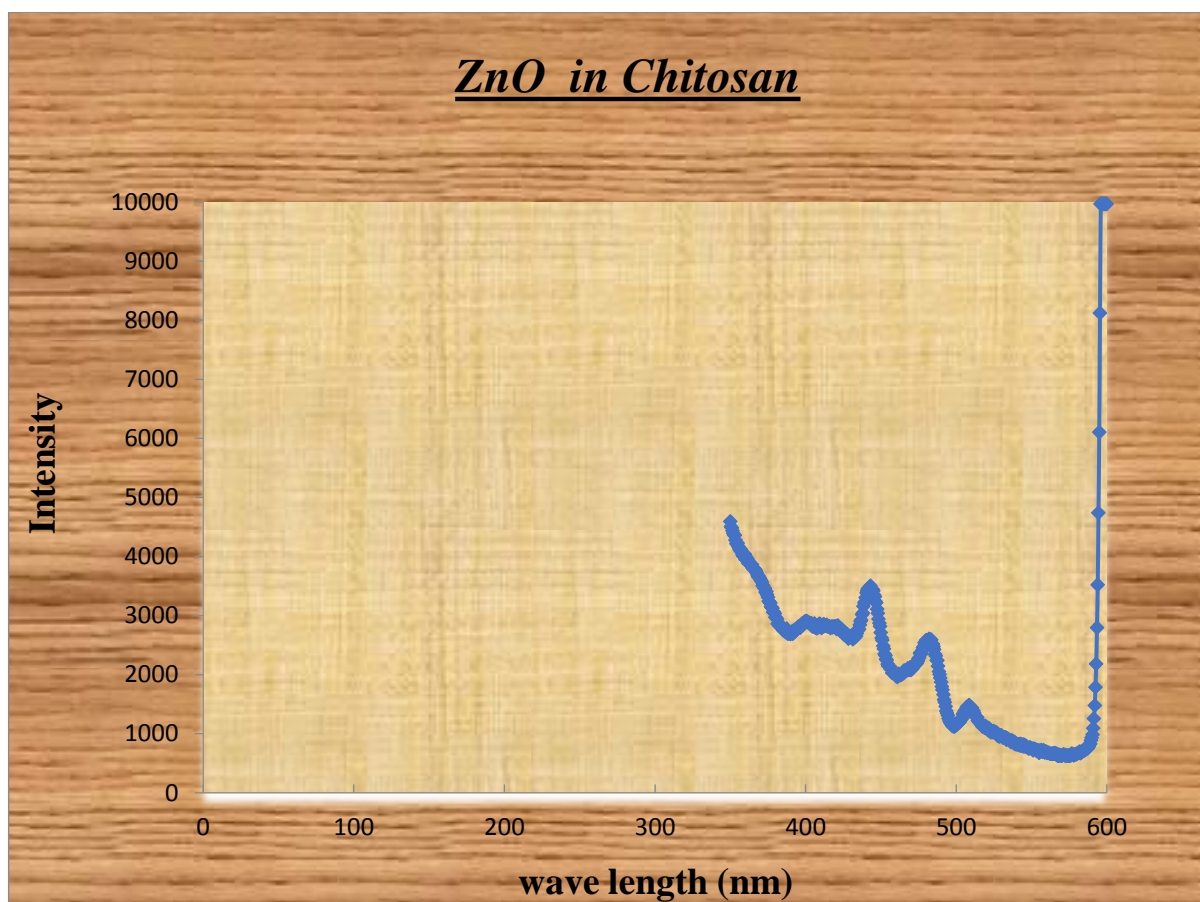


Figure 9a: ZnO in Chitosan

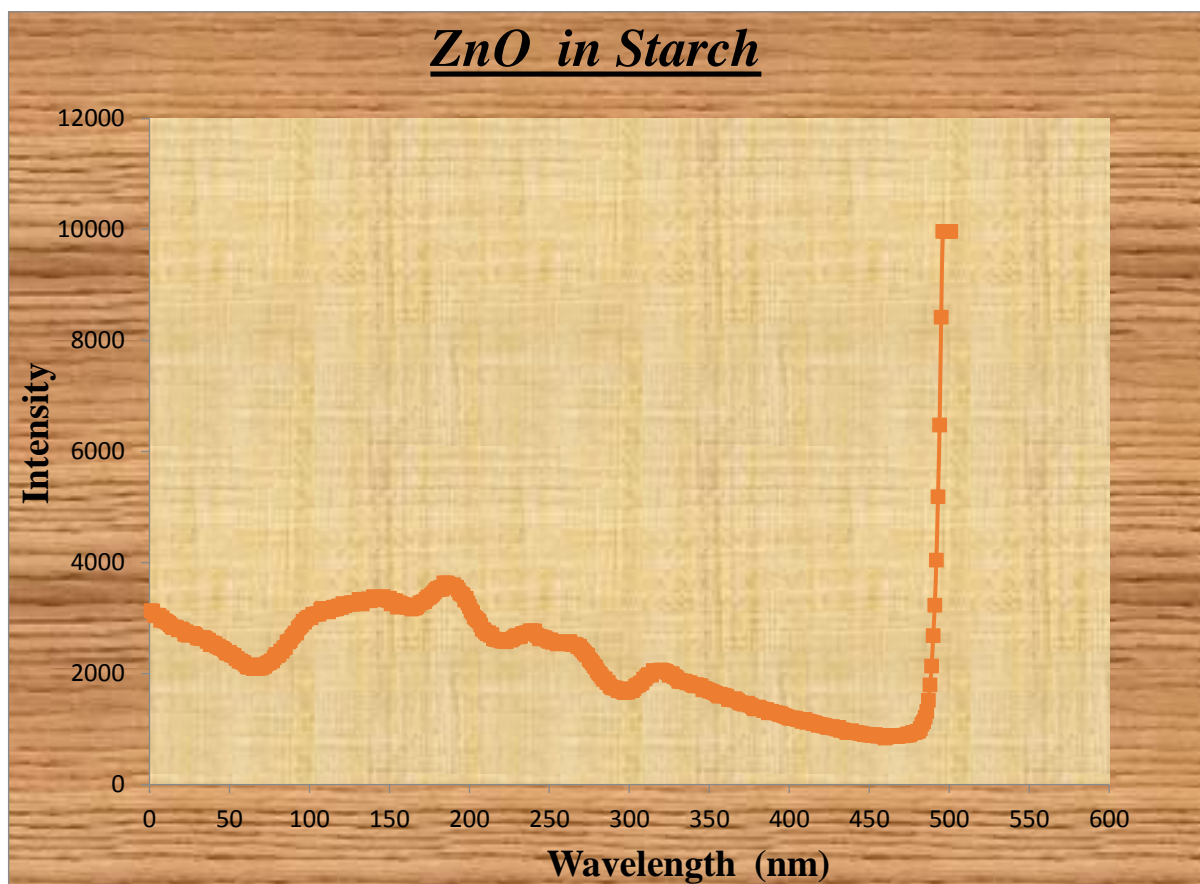


Figure 9b: ZnO in Starch

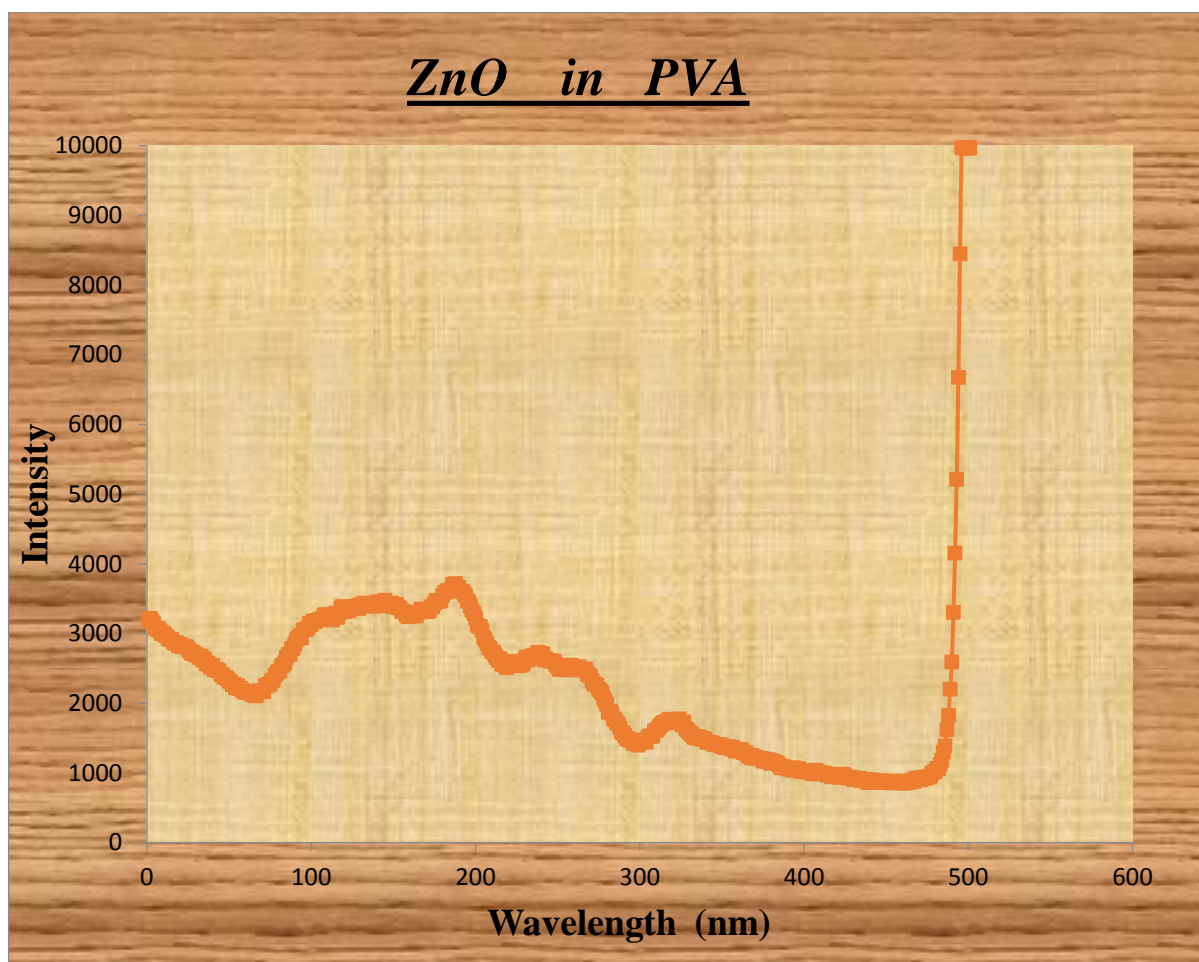


Figure 9c: ZnO in PVA

The luminescent properties of the samples depend on the preparation conditions of the samples. The green luminescence of ZnO nano structures may be due to vacancies at the nonpolar surfaces of the crystal structure²⁷. The chemical origin of these surface defects which have also been attributed to Zn/O vacancies, impurities, surface reconstructions, etc., is not generally agreed upon.

The results of the study indicate the determinant role of Zn vacancies (V_{Zn}) on the green luminescence of ZnO nanostructures. The study establishes the link and the origin of the green band to defects on the surface of the nanostructures³. This opens the door to managing and reducing unwanted charge recombination in optical and electronic devices such as photovoltaic systems and in enhancing the photocurrent and efficiency of the final product.

The nonstoichiometric defects such as oxygen vacancies connected to the Zn deposition or Zn interstitials, caused the fluorescence. Typically, these flaws cause a green fluorescence, albeit depending on the synthesis conditions. There may also be a minor blue or red shift. Thus, the fact that the ZnO nanoparticles we created showed red fluorescence, is extremely unusual and intriguing. Therefore, the method by which their complicated flaws and

inherent defects like zinc vacancies and oxygen vacancies formed; may have been very different. Strong defects-related emission at a shifted wavelength may have been caused by the different species and concentration of these defects⁸.

The determination of the chemical and/or crystallographic origin of the visible bands resulting from intra gap states in the emission spectra in nanostructured ZnO is the most contentious topic. Even though these optical contributions are generally attributed to the presence of defects, a precise assignment of them is still lacking. This is because both experimental studies of defect emissions and theoretical simulations of the electronic structure and formation energy of various defects have not yet produced a clear conclusion. ZnO-based devices have received a lot of interest and anticipation, but until recently, they have only really been commercialized for sensing applications. Poor doping control, particularly with regard to p-doping, recombination and contact stability, still place restrictions on other applications.

Conclusion

Nano-sized metal oxides with uniform shape and narrow size distribution are shown to possess many interesting properties not shown by their bulk counterparts. They have larger surface area and wider band gap between valence and

conduction bands. Nano ZnO exhibit excellent physical and chemical properties. Nano zinc oxide has a wide range of applications in various fields due to its unique and superior physical and chemical properties compared with bulk zinc oxide. The large specific surface area, high pore volume, low toxicity, nano structured properties and low cost of nano zinc oxide make it a promising candidate particularly as catalyst, chemical absorbents as polymer additives and advanced ceramics. Nano zinc oxide with higher crystallinity is successfully prepared by the *in situ* precipitation of ZnO in different polymeric medium like chitosan, starch and PVA. The characterization studies were done using XRD, SEM and particle size analyser.

It was found that nano ZnO prepared from the bio polymer mediums like chitosan and starch have almost similar crystalline shape and size whereas, nano ZnO prepared from synthetic polymer medium, PVA has slightly different structure and smaller particle size. The difference in structure and crystalline size may be due to the difference in structure of polymer-metal complex. Compared to chitosan and starch, PVA has low molecular weight and good water solubility, these two parameters enhance the stability of the complex formed. Luminescent properties of the ZnO from the three media show green luminescence but slightly differ in their corresponding wave length.

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