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PRECURSORS AND MEDIUM EFFECT ON ZINC OXIDE NANOPARTICLES SYNTHESIZED BY SOLGEL PROCESS

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ABSTRACT

The paper deals with the synthesis and characterization of ZnO Nanoparticles using XRD, SEM and FTIR .Stable OH free Zinc oxide(ZnO) Nanoparticles were synthesized by Sol-gel method by varying precursors in different mediums .The characterizations were performed using powder X Ray diffraction (XRD) for studying the crystal structure of ZnO ,Scanning electron microscopy (SEM) for capturing the images that contains the topographical information of nanoparticles and Fourier Transform Infrared (FTIR) Spectroscopy for identifying the name of chemical groups and bonds .The results, analysis and interpretations of four types of ZnO Nanoparticles (ZnO-1,ZnO-2, ZnO-3 and ZnO-4) were discussed.

KEYWORDS: FTIR, Nanoparticles, SEM, XRD, Zinc Oxide

INTRODUCTION

ZnO is an important II–VI compound semiconductor material due to its novel properties like large direct energy gap (3.37 eV), High melting point (2248 k) high refractive index, Large exiton B.E (60 mev) at room temperature. This semiconductor also exhibit several favorable properties like good transparency, high electron mobility, wide band gap, strong room temperature luminescence, high thermal conductivity, antibacterial and UV- protection. The powder could be used in many materials and including medicine, cosmetics, rubber, solar cells and foods is widely used as an additive into numerous materials and products including plastics, ceramics, glass, cement, rubber (e.g. car tyres), lubricants, paints, ointments, adhesives, sealants, pigments, foods (source of Zn nutrient), batteries, ferrites, fire retardants, etc. Zinc oxide has high biocompatibility and fast electric transfer kinetics, such phenomena encourage the use of this material as a biomimic membrane to immobilize and modify the biomolecules. In many literatures, it can be learned that nano ZnO offers better performance compared to that of bulk size. Recently ZnO is listed as generally documented as safe material by FDA (food and drug administration, (USA).

Many methods have been used to prepare ZnO nanoparticles like sol-gel method, thermal decomposition, chemical vapor decomposition (CVD) and alloy evaporation-deposition. A simple, fast wet chemical route based on cyclohexyl amine for synthesizing zinc oxide nanoparticles in aqueous and ethanolic media was established by Abdul-Aziz. Particles of polyhedra morphology were obtained for ZnO prepared in ethanol, while spherical and some chunky particles were obtained for zinc oxide prepared in water Bari (2009), has observed that when NH_4OH is used as the solvent for zinc acetate to synthesis nano ZnO particles, the particles are spherical, while the particles are wire like when sodium hydroxide is used as solvent. Also, the results of Zaborski (2010) revealed the morphology of ZnO which was prepared in the presence of the ionic liquids is spherical while it changes to plate-like without ionic liquids. It is demonstrated that ZnO with different morphologies such as flowers and rods can be controllable obtained by simply varying the basicity in the solution. Eric (1998) found that ZnO nanoparticles continue to grow after synthesis, even when stored at 0C°. The ability to obtain various particle sizes is based on this phenomenon. Also, it was found that the solution composition and temperature have a marked influence on the rate of the particle growth.

In brief, the solvents, temperature and media of experiment affect the particle size and particle morphology of synthesized ZnO nanoparticles. The aim of this research was to find a simple route to prepare nano ZnO particles via Sol- Gel method and characterize the final product using several techniques.

The sol-gel synthesis of ZnO powder has following advantages. Powder with nanometer- size different morphologies can be obtained with simple cost under moderate temperate. The properties are analyzed by performing various characterizations using XRD, SEM and FTIR spectroscopic techniques.

EXPERIMENTAL DETAILS

Chemicals

Zinc Chloride ($ZnCl_{2)}$, Zinc Nitrate ($Zn(NO_3)_2$, Potassium hydroxide(KOH) ,Sodium hydroxide (NaOH), Ethanol (C_2H_6O) and Distilled water were purchased and used without further purification. All chemicals used in the experiment are analytic reagent grade (AR grade)

Apparatus

Magnetic stirrer (REMI, MLH), Glass jars, Centrifuge Mission (REMI), Micro oven (VSE 230 A/C), High Precision Balance (INFRA)

EXPERIMENTAL PROCEDURE

Synthesis of ZnO Nanoparticles (ZnO-1, ZnO-2, ZnO-3, ZnO-4)

The Zinc oxide nanoparticles were synthesized using Sol-gel process varying the precursors in different mediums. In Alcoholic medium the ZnO-1, ZnO-2 Particles were synthesized while in the Hydrolysis medium ZnO-3 and ZnO-4 nanopowders were prepared. In the experiment procedure 0.4 M aqueous ethanol solution of $ZnCl_2$ was kept under constant stirring using magnetic stirrer to completely dissolve the zinc chloride 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 KOH 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 $ZnCl_2$ and KOH solutions in an aqueous alkaline solution results in immediate precipitation of ZnO, and the colour 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, $ZnCl_2$ is completely converted in to ZnO. The powder is solvents labeled as ZnO-1, following same procedure the ZnO-2 Nanoparticles were synthesized using Potassium hydroxide as precursor instead of Sodium Hydroxide in the above procedure.

In a similar manner, ZnO-3 and ZnO-4 Nanoparticles were synthesized by varying the precurors in Hydrolysis medium, Zinc Nitrate, KOH and Distilled Water as starting materials ZnO-3 Nanoparticles and Zinc Nitrate, NaOH and Distilled Water as precursors.ZnO-4 Nanoparticles were synthesized. Further, the samples of ZnO-1, ZnO-2, ZnO-3, ZnO-4 nanoparticles were characterized for their optical and nano-structural properties using X-ray diffraction, scanning electron microscopy and Fourier Transform Infrared (FTIR) Spectroscopy.

ZNO NANOPARTICLE CHARACTERIZATIONS

X-Ray Diffraction (XRD)

X-ray diffraction is now a common technique for the study of crystal structures and atomic spacing.

X-ray diffraction patterns for the ZnO nanoparticles were recorded using an X-ray diffractometer (PANLYTICAL) using secondary monochromatic CuK_{α} radiation of wavelength λ = 0.1541 nm at 40 Kv/50mA in the scan range 2θ = 20 to 90^{o}. Samples were supported on a glass slide.

Scanning Electron Microscopy (SEM)

Morphology of the samples were 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.

Fourier Transform Infrared (FTIR) Spectroscopy

The optical characterization of Nanopowder is performed using Fourier Transform Infrared spectroscopy (FTIR) .The presence of certain functional groups in a molecule can be obtained using FTIR.

RESULTS AND DISCUSSIONS

X ray Diffraction

The synthesized powders were primarily investigated by powder XRD; it is a non-destructive and analytical method for identification and quantitative analysis of various crystalline forms of ZnO, also known as phases of the compound present in the samples. From XRD patterns analyses, peak intensity, position and width, full-width at half-maximum (FWHM) data can be obtained

The size of the crystallites can be calculated using the Scherrer's formula

$P=0.9\ \lambda / \beta \cos\theta$

P - Crystallite size

λ – Wavelength (1.54 Armstrong) of incident x ray beam

β - Full Width half maxima in radians

θ – Scattering angle in Degree

Figure 1,2,3,4 and 5 show the XRD patterns of various ZnO nanoparticles. The diffraction patterns were recorded from 20° to 90° using CuKα (λ=1.542Ao). The XRD pattern indicates the pure wurtzite phase formation of ZnO without any impurity phase in all the samples. The broadening of the peaks reflects the nano-particle nature of the sample**.** In X-ray diffraction spectra, some prominent peaks were considered and corresponding d-values were compared with the standard [JCPDS file No. 80-0075]. The peaks represents that metal oxide is pure ZnO having hexagonal structure.

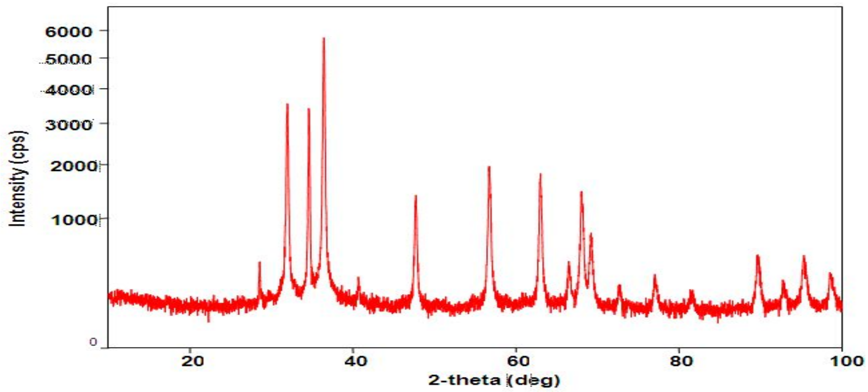

Figure 1: XRD Spectrum of ZnO-1 Nanopowders Synthesized in Alcoholic Medium

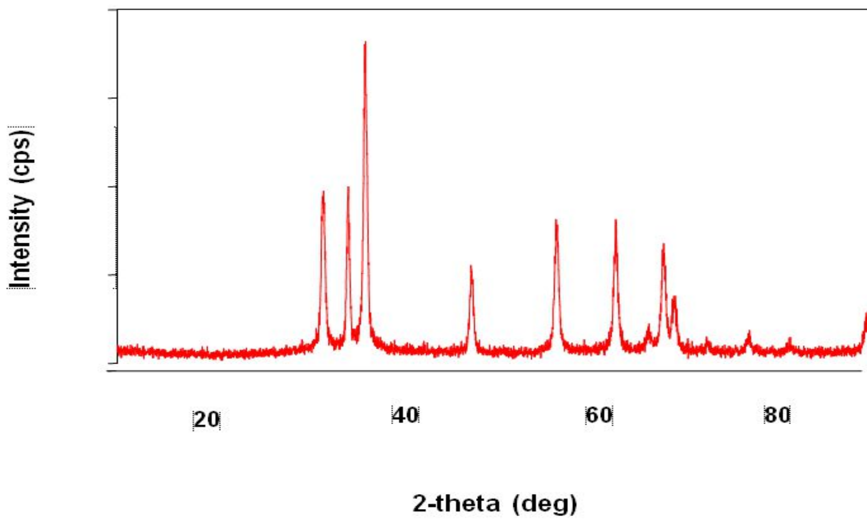

Figure 2: XRD Spectrum of ZnO-2 Nanoparticles Synthesized in Alcoholic Medium

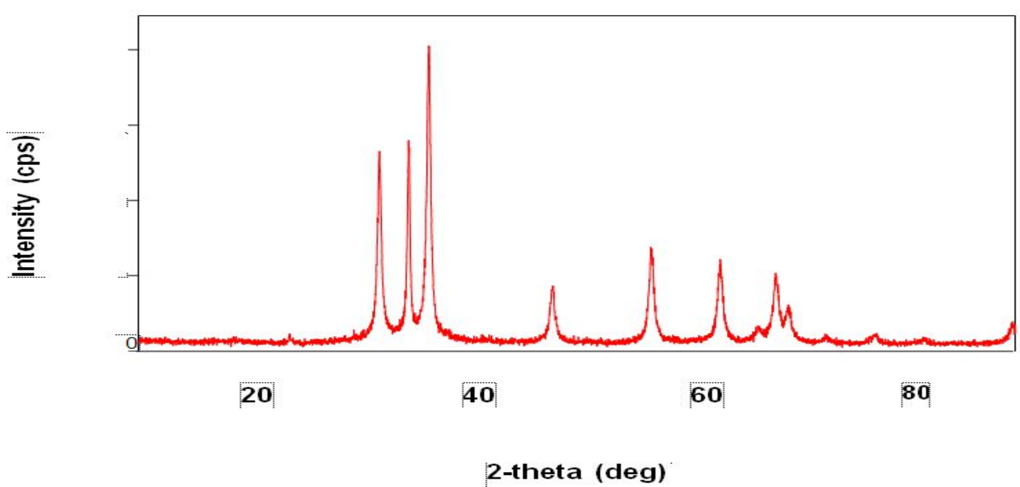

Figure 3: XRD Spectrum of ZnO-3 Nanoparticles Synthesized in Hydrolysis Medium

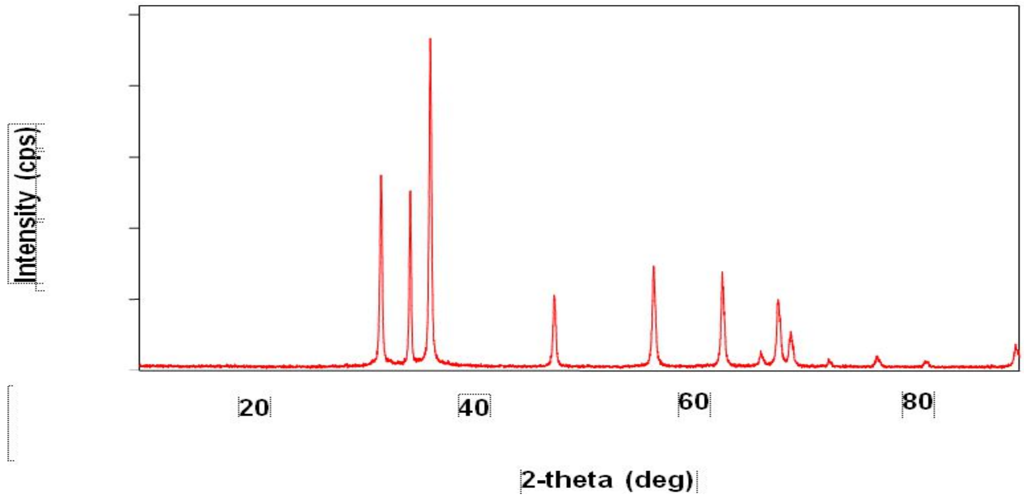

Figure 4: XRD Spectrum of ZnO-3 Nanoparticles Synthesized in Hydrolysis Medium

In Figure 1, the distinctive ZnO Peaks at 13.31º, 32.03º, 33.12º, 34.596º, 36.42º,56.62º,62.99º and 67.93º respectively. The full width at half maximum was measured using Gaussian curve for the highest Peak 101. Average particle size of the particles have been calculated from high intensity peak using the Scherer's formula is 10.05nm,The distortions in the XRD pattern may be due to the Strain Present in the sample

In Figure 2, The distinctive ZnO Peaks at 31.951º, 34.658º, 36.453º , 47.74º, 56.78 º, 62.99º, 66.38º, 68.06º , 79.96º respectively. The average particle size calculated from full width at half maximum for the high intensity Peak 101 using the Scherer's formula is 19.3 nm

In Figure 3, The distinctive ZnO Peaks at 31.946º, 34.631º, 36.448º, 47.755º, 56.769º, 62.928º, 66.45º, 68.09º, 69.19º , 77.17 º and 81.56º respectively. The average particle size calculated from full width at half maximum for the high intensity Peak 101 using the Scherer's formula is 19 nm.

In Figure 4,The distinctive ZnO Peaks at 31.946º, 34.631º, 36.433º, 47.692º, 56.736º, 62.987º, 66.51º, 68.055º, 69.116º, 72.656º and 77.02,81.41º and 89.667 respectively. The average particle size calculated from full width at half maximum for the high intensity Peak 101 using the Scherer's formula is 19.2 nm.

SCANNING ELECTRON MICROSCOPY

The structural morphologies of the synthesized powders were observed by SEM. As the surface to volume ratio is the dominant factor in nanostructured materials, probing the materials surface features is the prerequisite for many important applications. SEM micrographs of the zinc oxide NPs observed at different magnifications have been represented in the Figure 5. 6, 7 and 8 respectively. SEM studies shows the obtained nanopowders are in pure form with beautiful white colored nanoparticles

The micrographs clearly show the formation of Nanoparticles. From Figure 5, it is clear that ZnO-1 nanoparticles represent the morphology of nanoflakes arranged like flower like structure at different magnifications. Randomly oriented aggregates of nanoparticles with variable sizes can be observed in Micrographs of ZnO-2 Nanoparticles. Nanoflame like morphology in ZnO-3 nanoparticles Figure 2.4 shows the surface morphologies of ZnO-4 Nanoparticles form irregular spherical shape with narrow particle size distribution.

It is also observed that most of the particles exhibit some faceting. The SEM images represent the agglomeration of particles and also with narrow particle size distribution

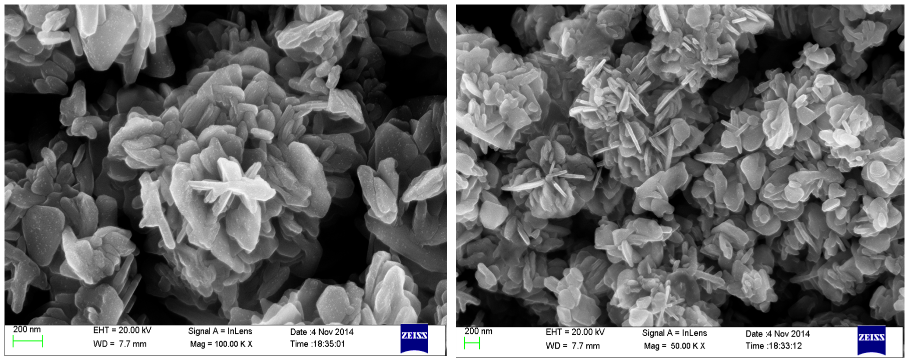

Figure 5: SEM Pictures of ZnO-1 Nanoparticles Synthesized in Alcoholic Medium

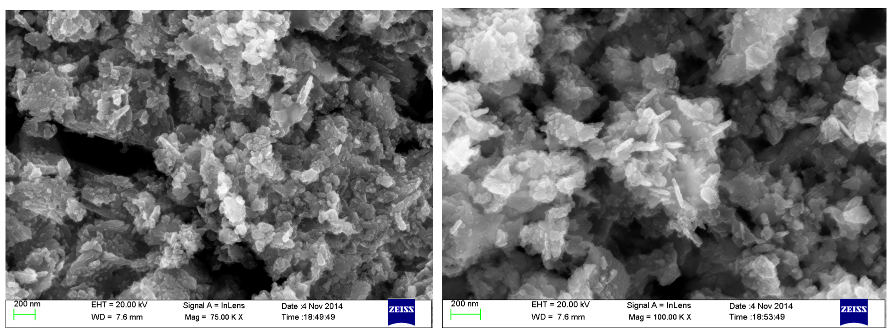

Figure 6: SEM Pictures of ZnO-1 Nanoparticles Synthesized in Alcoholic Medium

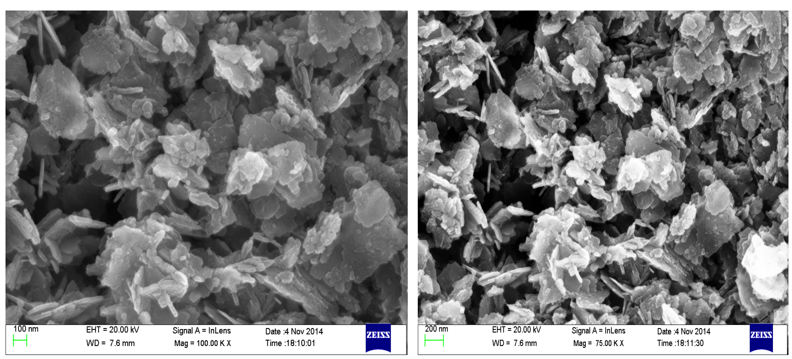

Figure 7: SEM Pictures of ZnO-1 Nanoparticles Synthesized in Hydrolysis Medium

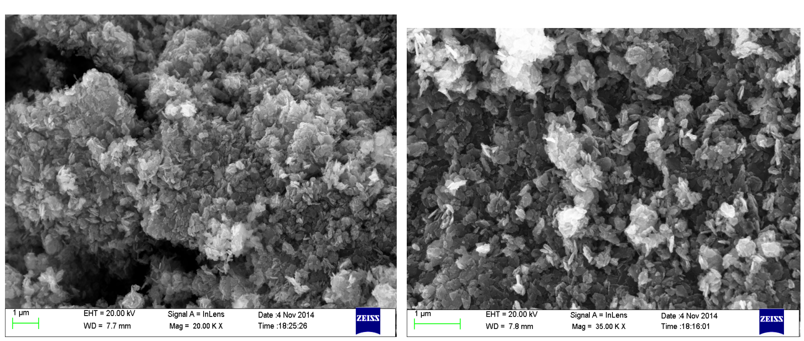

Figure 8: SEM Pictures of ZnO-1 Nanoparticles Synthesized in Hydrolysis Medium

FOURIER TRANSFORM INFRARED (FTIR) SPECTROSCOPY

FTIR is one of the widely used methods which is also known as Fourier Transform Infrared Spectroscopy used to identify the functional group which is present in certain molecules. The FTIR spectrum presented in the figures 9, 10, 11, 12 are performed to study the absorbance properties of znO nanoparticles, the spectrum contains absorption peaks in the range 4000-500 Cm-1.

From spectra, the absorption bands around 3400 cm-1 corresponds to OH bending to hydroxyl group, due to the water contents. The peaks form 1500-1600 cm-1 corresponds to CO group of carboxylic derivates, The peaks observed near 400-500 cm-1 are due to stretching mode of Zn-O ,The shifts observed may be due to the change in the bond length of Nzo Nanoparticles. The variation in the spectra of ZnO nanoparticles of FTIR spectra is due to the influence of Particle size and morphology particle size and morphology

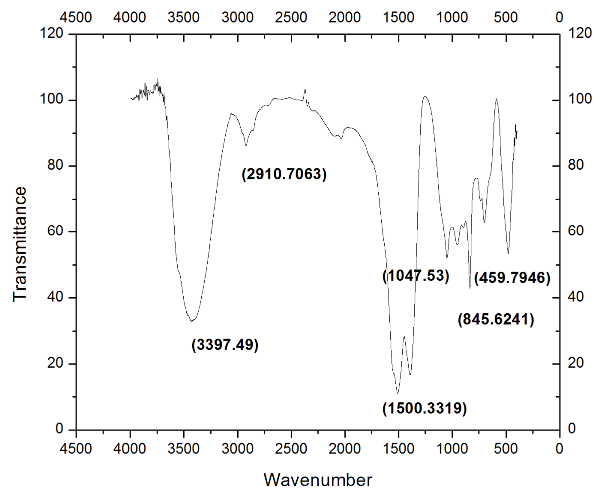

Figure 9: FTIR Pictures of ZnO-1 Nanoparticles Synthesized in Alcoholic Medium

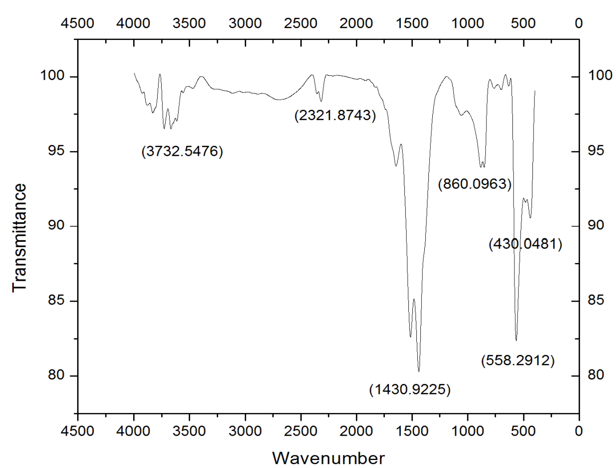

Figure 10: FTIR Pictures of ZnO-2 Nanoparticles Synthesized in Alcoholic Medium

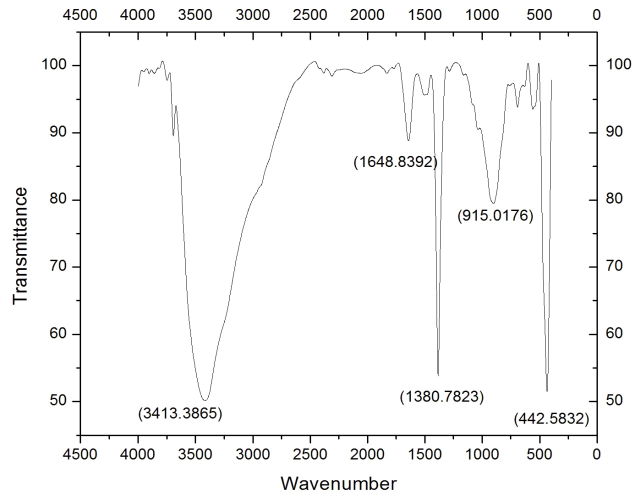

Figure 11: FTIR Pictures of ZnO-3 Nanoparticles Synthesized in Hydrolysis Medium

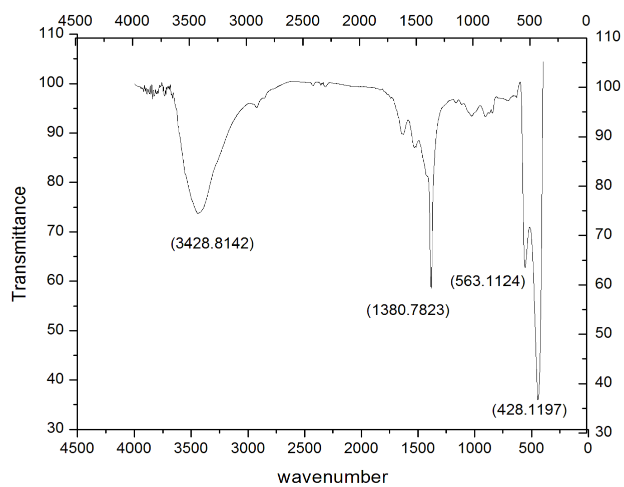

Figure 12: FTIR Pictures of ZnO-4 Nanoparticles Synthesized in Hydrolysis Medium

CONCLUSIONS

In this paper OH free ZnO Nanoparticles were successfully synthesized by simple, low-cost Sol-gel process varying precursors in different mediums. The structural and optical properties of nanoparticles were analyzed using XRD, SEM and FTIR characterizations. XRD revealed hexagonal wurtzite structure of ZnO nanoparticles. The chemical groups in the samples have been identified by FTIR spectra .SEM images showed the morphology of particles is influenced by precursors and medium. These ZnO nanoparticles can be used in different industrial applications viz., luminescent material for fluorescent tubes, active medium for lasers, sensors etc.

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