Investigation on the Sol-Gel Synthesis, Morphology and Characterization of Zinc Oxide Nanoparticles

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ABSTRACT

ZnO nanoparticles have been synthesized by SOL-GEL process from zinc nitrate. The powder was characterized by X-ray diffraction, scanning electron transmission. XRD patters showed that ZnO nanoparticles have hexagonal unit cell structure. SEM pictures reveal the morphology and particle size of prepared ZnO nanoparticles. The synthesis method has potential for application in manufacturing units due to ease processing and more economical reagents.

KEYWORDS: Z_NO , Nano, Scanning electron transmission

1. INTRODUCTION:

Nano means 10^{-9}. A nanometre is 1000 millionth of a metre. Atoms are extremely small and the diameter of a single atom can vary from 0.1-0.5 nm depending on type of element. For example one carbon atom is approx. 0.15 nm diameter. The radius of one atom can be considered as half the distance between neighbouring atoms when they are present in the solid phase. To understand how small 1 nm is let us see few comparisons. A red blood cell is approx. 7000 nm wide and a water molecule is among 0.3 nm across. Quite often people make a comparison with human hair which is about 8000 nm wide.

2. Synthesis of ZnO Nanoparticles:

The ZnO nanoparticles will prepared by wet chemical method using zinc nitrate and sodium hydroxides precursors and soluble starch as stabilizing agent. Soluble starch will dissolved in distilled water and treated in microwave oven (Samsung, Model No- CE103VD) for complete solubilisation. Zinc nitrate, added in the above solution. Then the solution will keep under constant stirring at room temperature using magnetic stirrer (Tarson spinnot digital) for one hour. After complete dissolution of zinc nitrate, sodium hydroxide solution will add under constant stirring, drop by drop touching the walls of the vessel. The reaction will allow proceeding for 2 h after complete addition of sodium hydroxide. After the completion of reaction, the solution is allowed to settle for overnight and the supernatant solution was then discarded carefully. The remaining solution centrifuged (Remi cooling centrifuge instrument, Model No-C30BL) at 10,000 × g for 10 min and the supernatant will discard. Thus produced nanoparticles wash three times using distilled water. Washing carried out to remove the by-products and the excessive starch bound with the nanoparticles. After washing, the nanoparticles are dried at 80°C for overnight. During drying, complete conversion of Zn (OH) 2 into ZnO takes place.

2.1. Characterization Techniques:

2.1.1. Scanning Electron Microscope (SEM):

The scanning electron microscope uses a beam of high-energy electrons to produce a variety of signals at the surface of specimens used. The signals show information about the sample including chemical composition, and crystalline structure, external morphology (texture) and orientation of materials which make up the sample.

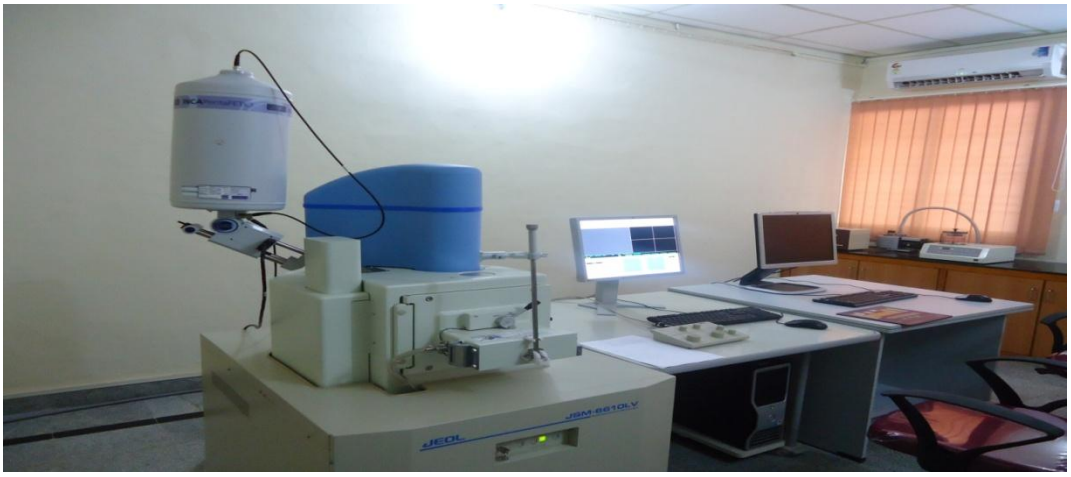

Fig.1: SEM (JEOL-JSM 5800)

SEM analysis is normally considered to be non-destructive because the x-rays generated do not lead to loss of volume of the sample, so it becomes possible to repeatedly analyze the same materials. A scanning electron microscope is a kind of electron microscope which images a sample by scanning it using a high-energy electron beam. The electrons then interact with the atoms making up the sample, thus producing signals which reveal information about the sample's composition, surface topography and other properties such as electrical conductivity.

Various types of signals produced by a SEM include back-scattered electrons (BSE), secondary electrons, characteristic X-rays, specimen current, light (cathodoluminescence) and transmitted electrons. Back-scattered electrons (BSE) are the electrons which are reflected by elastic scattering from the sample. Because the intensity of the BSE signal is related to the atomic number of the specimen, BSE images can provide information about the different elements distribution in the sample very accurately. Characteristic X-rays are released when the electron beam removes an electron from the inner shell of the sample, thus causing a higher energy electron to occupy the shell and hence release energy in the form of X-rays. These characteristic X-rays are in turn used to find out the composition of the material and also measure the presence of elements in the sample as well as the level of impurities.

Magnification in a scanning electron microscope technique can be controlled over a range of about 6 orders of magnitude from approximately 10 to 500,000 times. Assuming that the display screen has a fixed size, higher magnification is obtained by reducing the raster size of the specimen, and vice versa. Magnification is hence controlled by the voltage supplied to the x, y deflector plates or the current supplied to the scanning coils and not by objective lens power.

2.1.2. Particle Size Analyzer:

Particle size of the milled powder is measured by Malvern particle size analyzer (Model Micro-P, range 0.05-550 micron). Firstly, the liquid dispersant containing 500ml 0f distilled water and 25 ml of sodium hexametaphosphate are keep in the sample holder. Then the instrument is run keeping ultrasonic displacement at 10.00 micron and pump speed 1800 rpm.

A pinch of powders are added to the liquid dispersant so that the obscuration value varies between 10 to 30% and the residual below 1%.

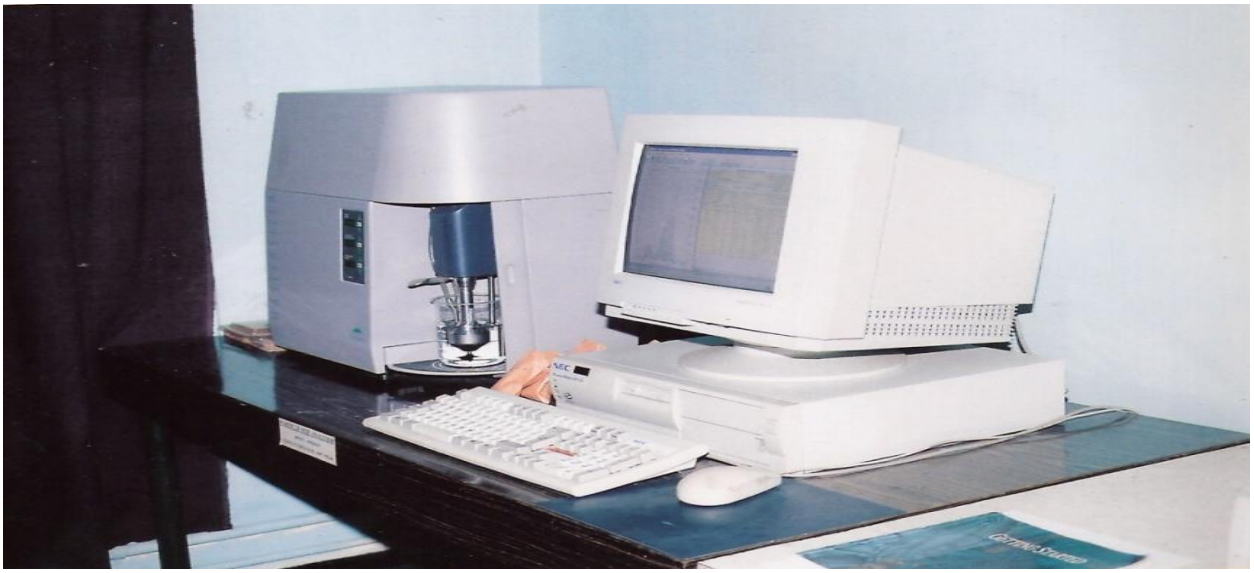

Fig.2: Malvern particle size analyzer (Model Micro-P, range 0.05-550 micron).

2.1.3. Energy Dispersive X-ray Spectroscopy:

Energy dispersive X-ray spectroscopy (EDS, EDX or EDXRF) is an analytical technique used for the elemental analysis or chemical characterization of a sample. It is one of the variants of XRF. As a type of spectroscopy, it relies on the investigation of a sample through interactions between electromagnetic radiation and matter, analyzing x-rays emitted by the matter in response to being hit with charged particles. Its characterization capabilities are due in large part to the fundamental principle that each element has a unique atomic structure allowing x-rays that are characteristic of an element's atomic structure to be identified uniquely from each other.

To stimulate the emission of characteristic X-rays from a specimen, a high energy beam of charged particles such as electrons or protons (see PIXE), or a beam of X-rays, is focused into the sample being studied. At rest, an atom within the sample contains ground state (or unexcited) electrons in discrete energy levels or electron shells bound to the nucleus.

The incident beam may excite an electron in an inner shell, ejecting it from the shell while creating an electron hole where the electron. An electron from an outer, higher-energy shell then fills the hole, and the difference in energy between the higher-energy shell and the lower energy shell may be released in the form of an X-ray. The number and energy of the X-rays emitted from a specimen can be measured by an energy dispersive spectrometer. As the energy of the X-rays are characteristic of the difference in energy between the two shells, and

of the atomic structure of the element from which they are emitted, this allows the elemental composition of the specimen to be measured.

The excess energy of the electron that migrates to an inner shell to fill the newly created hole can do more than emit an X-ray. Often, instead of X-ray emission, the excess energy is transferred to a third electron from a further outer shell, prompting its ejection. This ejected species is called an Auger electron, and the method for its analysis is known as Auger Electron Spectroscopy (AES).

X-ray Photoelectron Spectroscopy (XPS) is another close relative of EDS, utilizing ejected electrons in a manner similar to that of AES. Information on the quantity and kinetic energy of ejected electrons is used to determine the binding energy of these now-liberated electrons, which is element-specific and allows chemical characterization of a sample. EDS is often contrasted with its spectroscopic counterpart, WDS (Wavelength-Dispersive X-ray Spectroscopy). WDS differs from EDS in that it uses the diffraction patterns created by lightmatter interaction as its raw data. WDS has a much finer spectral resolution than EDS. WDS also avoids the problems associated with artifacts in EDS (false peaks, noise from the amplifiers and microphonics. In WDS only one element can be analyzed at a time, while EDS gathers a spectrum of all elements, within limits, of a sample.

3.PROCEDURE FOR SYNTHESIS OF ZNO NANOPARTICLES:-

The ZnO nanoparticles are prepared by using Sol-Gel method. The reason behind choosing this method to make the nanoparticles is that it is the cheapest of all the remaining methods and free of pollution.

- In this synthesis process, Zn $(No_3)_2$ ($ZnCl_2$) is dissolved in ethanol by taking the required molarity (0.05M) under magnetic stirring.
- NaOH (KOH, Na2Co3) is dissolved in ethanol to the required molarity (0.2M) under magnetic stirring.
- These mixtures are mixed for around 45 to 60 minutes.
- For mixing KOH and Na_2CO_3 mixture in Zn $(No_3)_2$ mixture a doping agent is used.

Fig.3: Stirring of the two mixtures ($Zn(NO_3)_2$ and precursor KOH)

- Here the doping agent we used is cupric nitrate.
- This doping agent is dissolved in ethanol to the required molarity (0.1M) under magnetic stirring.
- Then we add ($Zn(NO_3)_2$ mixture drop by drop touching the walls of the vessel to NaOH (KOH, Na_2CO_3) mixture in a funnel under magnetic stirring.
- This mixture is then stirred for around 45 to 60 minutes.

Fig.4: Adding of both mixtures in the funnel

- Then if required we add the mixture of doping agent to the mixture drop by drop touching the walls of the vessel which is already prepared.

Fig.5: stirring the final mixture

- Then this final mixture is stirred for 45 minutes and taken into centrifuge test tubes.
- These test tubes are then placed in a centrifuge machine.
- These test tubes are then centrifuged for 10 to 15 minutes.

Fig.6: centrifuge process

- This process separates the solvent and precipitate in the test tube.
- Then test tubes are taken out for dropping out the solvent leaving the precipitate at the bottom.
- This process is repeated till no solvent comes from the test tubes.

Fig.7: Hot Air Oven

- Then remaining mixture in the test tubes is allowed to settle down for overnight and the next day these test tubes are again placed in centrifuge machine to remove the remaining solvent.
- Then these test tubes are placed in an oven to make the precipitate dry.
- The dry precipitate is then grinded by means of hand and then stored.

Fig.8: Packed Samples

RESULTS AND DISCUSSIONS

4.Structural and Morphological Analysis:

4.1.XRD Analysis of (Zn $(NO_3)_2$ + NaOH) Sample:

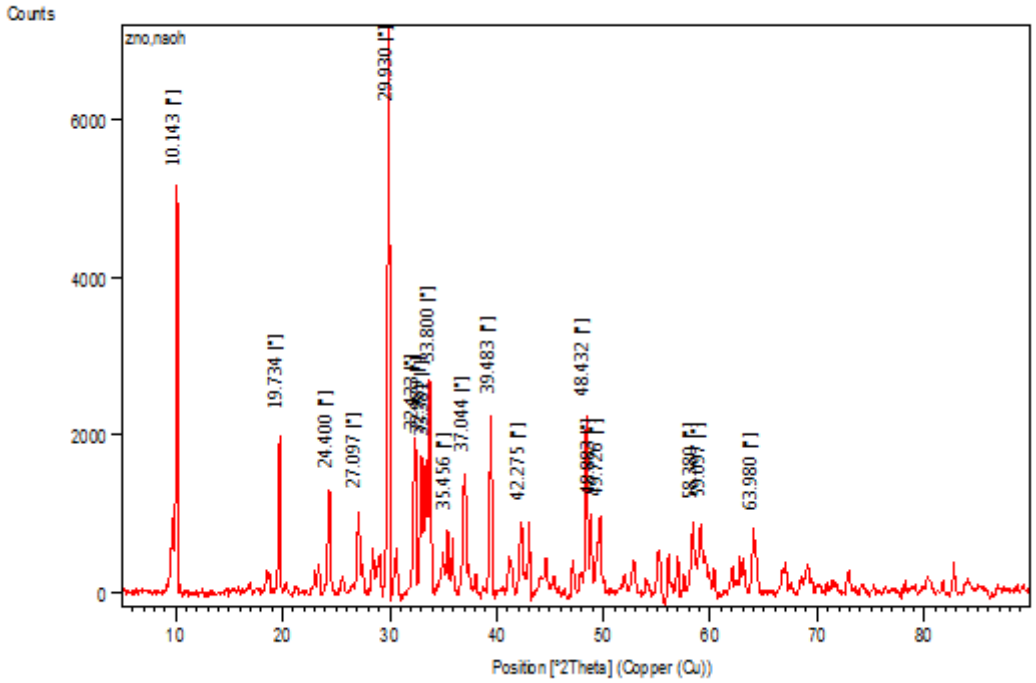

Fig.9: XRD pattern of ZnO sample

Fig. 13 represents the X-ray diffraction pattern of ZnO nano powder. A definite line broadening of the XRD peaks indicates that the prepared material consist of particles in nano scale range. From this XRD patterns analysis, we determined peak intensity, position and width, full-width at half-maximum (FWHM) data. The diffraction peaks located at The peak observed at 2θ = 10.14°, 19.73°, 24.39°, 27.09°, 29.93°, 33.80° and 39.48° correspondence to the height (cts): (5106.47), (2003.18), (1278.52), (1018.92), (7183.91), (2618.03) and (2231.87) respectively have been keenly indexed as hexagonal wurtzite phase of ZnO [28, 29] with lattice constants a=b= 0.324 nm and c= 0.521 nm (JPCDS card no: 36-1451) [30] and further it also confirms the synthesized nano powder was free of impurities as it does not contain any characteristics XRD peaks other than ZnO peaks. The synthesized ZnO nanoparticle diameter was calculated using Debye-Scherrer formula

$$d = \frac{0.89\lambda}{\beta Cos\ \theta} \qquad (1)$$

Where 0.89 is Scherrer's constant, λ is the wavelength of X-rays, θ is the Bragg diffraction angle and β is the full width at half-maximum (FWHM) of the diffraction peak corresponding to plane <101>. The average particle size of the sample was found to be 8nm which is derived from the FWHM of more intense peak corresponding to 101 plane located at 29.93° using Scherrer's formula.

3.1. XRD Analysis of (Zn $(NO_3)_2$ + KOH + CUO) Sample:

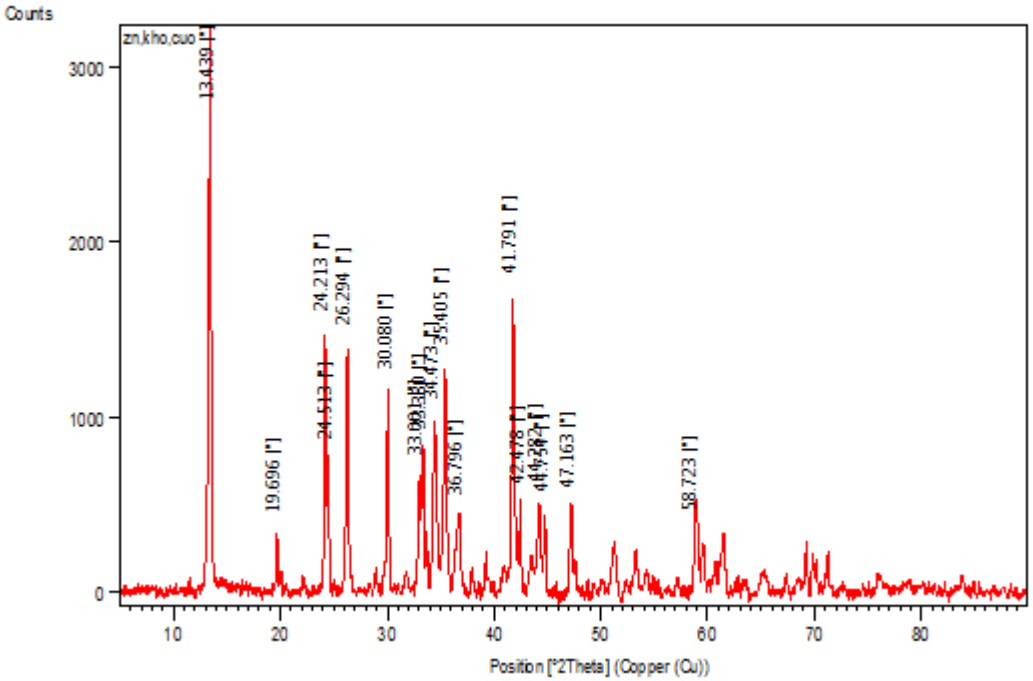

Fig.10: XRD pattern of ZnO sample

Fig. 14 represents the X-ray diffraction pattern of ZnO nano powder. A definite line broadening of the XRD peaks indicates that the prepared material consist of particles in nano scale range. From this XRD patterns analysis, we observed that the sample is highly crystalline as evident from the XRD pattern in which broad peaks with high intensity extended over the 2θ scale. The peak observed at 2θ = 13.43°, 24.21°, 24.51°, 26.29°, 30.08°, 35.40° and 41.79° correspondence to the height (cts): (3079.22), (1468.66), (739.65), (1388.63), (1117.97), (1275.82) and (1688.37) respectively, indicative of wurtzite hexagonal

structure of ZnO. The boarding of the peaks gives an idea about the small particle size of the synthesized ZnO.

The synthesized ZnO nanoparticle diameter was calculated using Debye-Scherrer formula

$$d = \frac{0.89\lambda}{\beta Cos\ \theta} \qquad (1)$$

where 0.89 is Scherrer's constant, λ is the wavelength of X-rays, θ is the Bragg diffraction angle and β is the full width at half-maximum (FWHM) of the diffraction peak corresponding to plane <101>. The average particle size of doped ZnO of the sample was found to be 10 nm which is derived from the FWHM of more intense peak corresponding to 101 planes located at 30.08° using Scherrer's formula.

3.2. SEM Micrographs of (Zn $(NO_3)_2$ + NaOH) Sample:

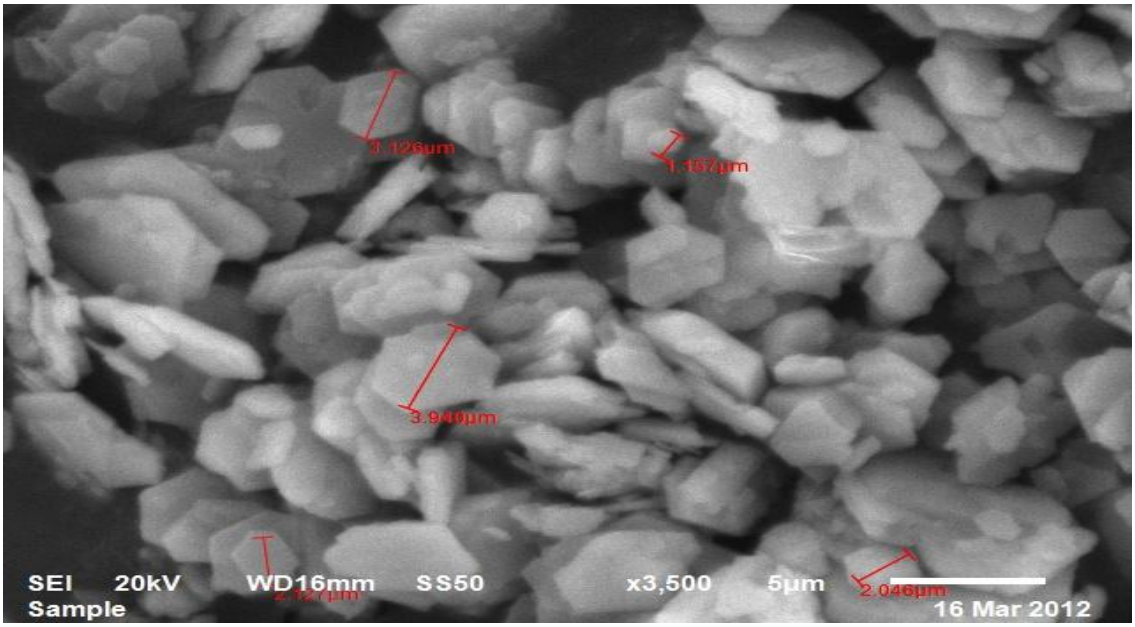

Fig.11: SEM image of ZnO at 3500x

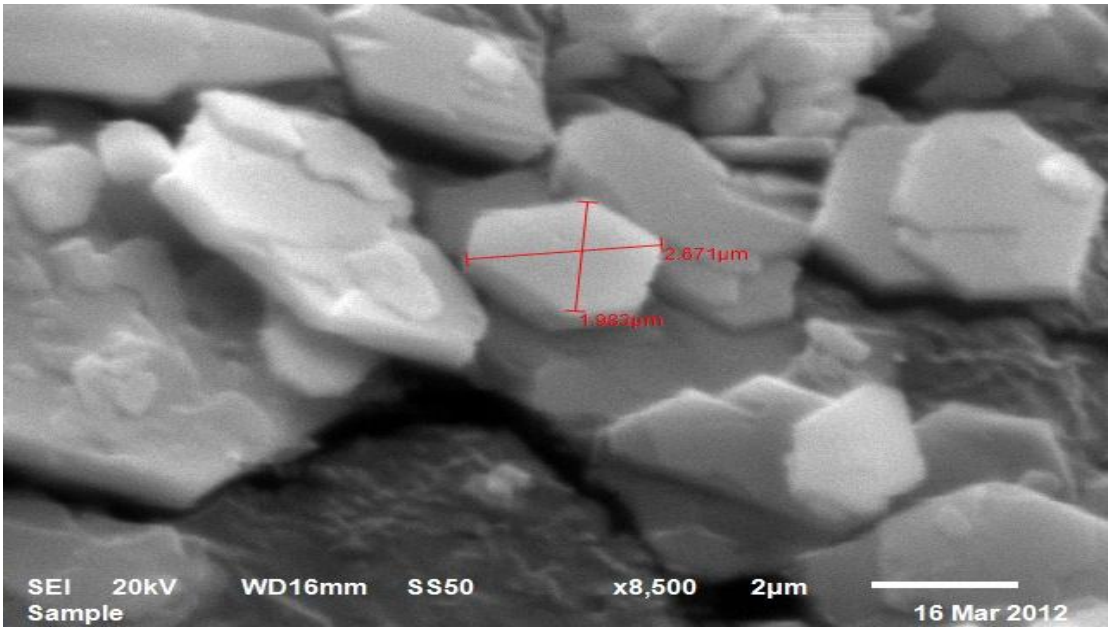

Fig.12: SEM image of ZnO at 8500x

SEM micrographs of the synthesized ZnO are shown in the figure 15 & 16. These pictures confirm the formation of ZnO nanoparticels. These pictures substantiate the approximate spherical shape to the nanoparticles and most of the particles exhibit some faceting. As the particle size calculated from the XRD is in nano range we are not getting any exact information about the surface morphology of the sample from the SEM micrograph, because of the limitation of our instruments up to micro range. The morphology observed in the sample shows the fine grains of ZnO which are of size 1.1~3.9 µm.

3.3. SEM Micrographs of (Zn $(NO_3)_2$ + KOH + CUO) Sample:

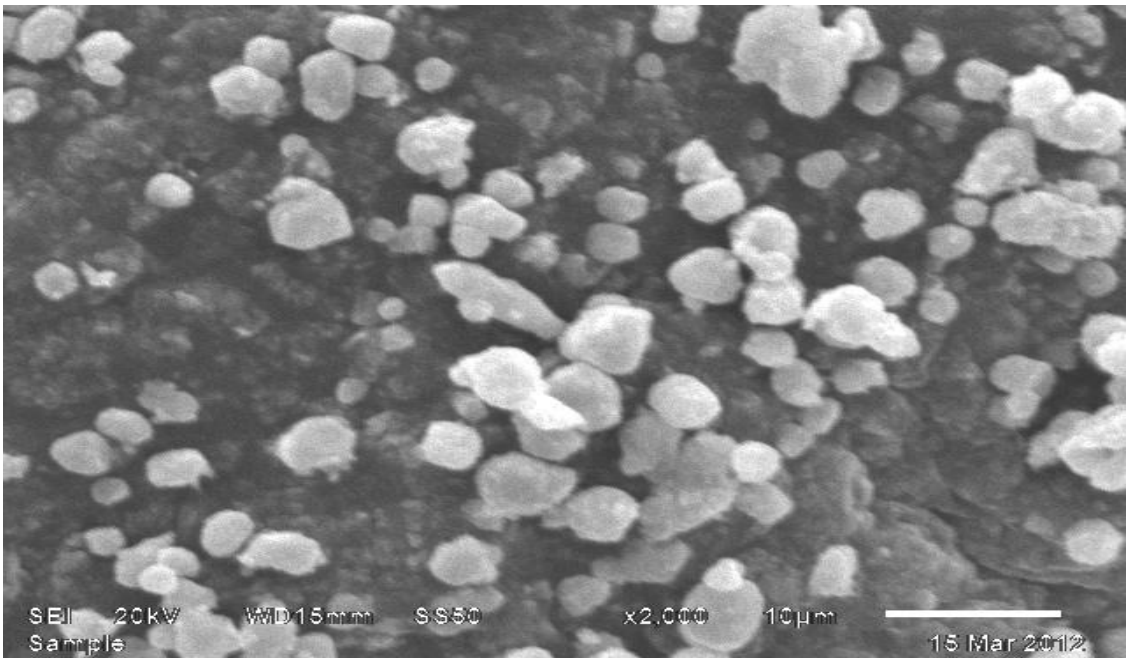

Fig.13: SEM image of ZnO at 2000x

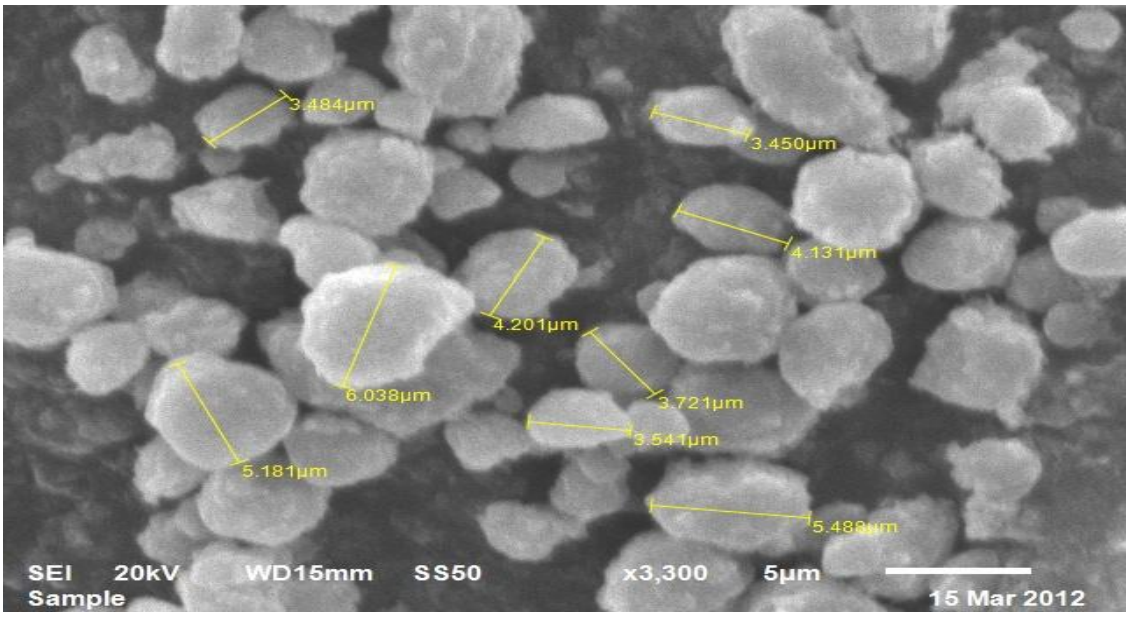

Fig.14: SEM image of ZnO at 3300x

SEM micrographs of the synthesized doped ZnO nanoparticles are shown in the figure 17 & 18. These pictures confirm the formation of ZnO nanoparticels. These pictures substantiate the approximate spherical shape to the nanoparticles and most of the particles exhibit some faceting. As the particle size calculated from the XRD is in nano range we are not getting any exact information about the surface morphology of the sample from the SEM micrograph,

because of the limitation of our instruments up to micro range. The morphology observed in the sample shows the fine grains of doped ZnO which are of size 3.4~6 µm.

5.CONCLUSION:

In this report, we have done synthesis of ZnO nanostructures using a single- step and low cost sol-gel process and were characterized by XRD, SEM.

The powder XRD pattern confirmed the structure of the obtained product. SEM images show the formation of spherical particles of sizes between 3-6 µm (approximately 8-10 nm).

The sol-gel route employed in this work is simple, cost effective and free of pollution and therefore, the technique can be extended to prepare many other important semiconducting metal oxide nanoparticles.

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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INTERNAL EXAMINER **EXTERNAL EXAMINER**

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ABSTRACT

ZnO nanoparticles have been synthesized by SOL-GEL process from zinc nitrate. The powder was characterized by X-ray diffraction, scanning electron transmission. XRD patters showed that ZnO nanoparticles have hexagonal unit cell structure. SEM pictures reveal the morphology and particle size of prepared ZnO nanoparticles. The synthesis method has potential for application in manufacturing units due to ease processing and more economical reagents.

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