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A Comparative Study of Zinc Oxide Nano Particles Synthesized by Hydrothermal, Sol-gel and Thermal Decomposition

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Abstract

In the proposed work, Zinc oxide nano particles (ZnO NP's) are synthesized using three different methods: Hydrothermal, Sol-gel and Thermal decomposition. The samples are characterized using X-ray diffraction (XRD), UV visible spectroscopy (UV-Vis), Fourier Transform Infrared Spectroscopy (FT-IR) and scanning electron microscopy (SEM). The XRD pattern exhibit single-phase polycrystalline nature of all the samples exhibiting the most intense peak at (101). The diffraction peaks are located at 31.80, 34.46, 36.28, 47.60, 56.62, 62.98, 68.04, 69.16 and 77.00 and have been keenly indexed as hexagonal wurtzite phase of ZnO. The FT-IR Spectra of ZnO NP's is recorded in the wave number range from 400 to 4000 cm^{-1}. In UV visible Spectra of ZnO absorption edge for sol-gel is around 345 nm, 360 nm for hydrothermal and shifted to 376 nm for thermal decomposition, which shows the increase in crystalline size. The energy band gap of materials is calculated using a well-known Tauc's plot from which the values E_g for all the three samples are for sol-gel E_g = 2.78 eV, thermal decomposition E_g = 2.90 eV and hydrothermal E_g = 3.20 eV. SEM images exhibit the formation of large spherical Nano particles for sol-gel method, Wurtzite structure for thermal decomposition and Nano rods in hydrothermally synthesized ZnO sample.

Keywords: Zinc oxide, Nano particles, Hydrothermal, Sol-gel, Thermal decomposition

INTRODUCTION

Nanotechnology means use of materials which are of Nano scale measurement. Nano scale particles have large surface area to volume ratio thereby exhibiting unique properties like thermal conductivity, catalytic reactivity, and optical properties. Metal oxide nanoparticles belonging to inorganic nanomaterial's such as Magnesium oxide (MgO), Titanium oxide (TiO_2), Copper oxide (CuO), Silver oxide (Ag_2O), Zinc oxide (ZnO) all are under research since from past few years. Among these metal oxides, ZnO has drawn great interest in past few years of research in the field of electronics, optics, biosensors, drug carriers, cosmetic ingredients, dental filling, biomedical areas, photo catalysis, electro technology industries and environmental protection [1–8]. In textile industry zinc oxide nano particles shows eye-catching functions of UV and visible light resistance [9]. ZnO nanoparticles are multifunctional material and have gained significant industrial interest due to their structural stability in different environments and it can easily fabricate at low temperature. Zinc oxide has noticeable features like large surface area, high surface reactivity. ZnO NP's have greater antibacterial, antimicrobial, and excellent UV-blocking properties, it has also arose a promising potential in the field of biomedicine especially in the field of diabetics and anticancer field. ZnO NPs were first used by rubber industry as they are

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having high polymer in their toughness and intensity and antiaging and other functions [10] US Food and Drug Administration (FDA) has listed ZnO NP's as GRAS (generally recognized as safe), inexpensive to produce and can be prepared easily [11]. Zinc Oxide has diameters less than 100 nanometers. It is an important n-type SC with a direct wide Energy band gap (3.37 eV-3.6 eV) and had large exiton binding energy of 60 meV at room temperature [12]. ZnO has good electron transport properties, and have high transparency at room temperature; therefore it shows properties like pyro electricity and piezoelectricity which makes it versatile and functional material. ZnO compound has gained attention in various fields, including medical and environmental applications as it is bio safe, biodegradable and biocompatible [13]. ZnO crystallizes in two main forms, cubic zinc blende and hexagonal wurtzite. Generally ZnO has hexagonal wurtzite structure. There are various methods for the synthesis of nanoparticles like physical method involving physical forces which requires costly equipment working at high temperature and pressure. Second method is chemical method which involves the use of toxic chemicals that are harmful environment and for the person who is handling it. ZnO NP's can be synthesized by various methods such as chemical vapor decomposition (CVD), amorphous crystallization, SOL-GEL, solvo thermal, hydrothermal, electro-deposition and biometric approaches. In this work three ways namely sol-gel, hydrothermal and thermal decomposition methods are used to study the crystal nature, energy band gap, surface morphology and vibrational band structure.

MATERIALS AND METHOD

For the synthesis of zinc oxide nanoparticles (ZnO NP's), precursor used are AR grade zinc acetate ($Zn(CH_3CO_2)_2.2H_2O$) for thermal and zinc nitrate ($Zn(NO_3)_3.6H_2O$) for sol-gel. In the hydrothermal process, zinc acetate $Zn(CH_3COO)_2$ is added with distilled water, ethylene glycol and NaOH then stir it continuously for 10 minutes. The obtained solution is put in the autoclave which is maintained within a furnace at a temperature of 200°C for duration of 12 hours. The sample is cooled at room temperature; the solute is subjected to filtration and undergoes multiple washes using ethanol. The sample undergoes an additional step wherein it is once again placed inside an oven set at a temperature of 100°C for duration of 12 hours. Resulting sample is then ground for one hour; afterwards it is subjected to a calcination process at a temperature of 600°C for a period of 4 hours, then after grinding the powdered form of sample is prepared. For Sol-Gel synthesis zinc nitrate ($Zn(NO_3)_3.6H_2O$) mixed with distilled water, ethylene Glycol and few drops of ammonia solution to maintain the pH of the sample. The obtained solution is put on magnetic stirrer for 6 hours. Then it is placed in a furnace at 200°C for 4 hours, and the prepared gel was dried for 12 hours at 80°C and calcined at 450°C for 6 hours, after grinding the powdered form of sample is ready. For thermal, zinc acetate ($Zn(CH_3CO_2)_2$. Mixed with distilled water is taken in first beaker and in another citric acid diluted with distilled water is taken both the beakers the placed on different magnetic stirrer at 70°C. Solution from second beaker is added to first dropwise, add ethylene Glycol and ammonia till PH reaches 7. The sample is placed in a furnace at 200°C for 4 hours after that it is grind and again sample is put in furnace at 450°C for 2 hours. Finally, the obtained sample is ground for an additional 20 minutes before proceeding with the characterizations. X-ray diffraction (XRD) analysis is then performed for the entire above prepared sample. By using Bruker Tenser 37 spectrometer, Fourier Transform Infrared (FTIR) spectroscopy recorded the spectra at wave number range of 400–4000 cm^{-1}. In U-V-Visible, the absorption edge spectra of ZnO nanoparticles are observed from 300–380 nm and it is analyzed by using Lambda 850, PerkinElmer spectrophotometer [14]. SEM (Model No. JSM 6510 LV, Make – JEOL, Japan) coupled with energy dispersive X-ray spectrometer (EDS) technique is used to study the surface morphology and element identification of ZnO Nano particles.

RESULTS AND DISCUSSION

Figure 1 depict the XRD patterns of ZnO samples prepared via thermal decomposition processes, definite line broadening of XRD peaks indicates that the prepared material has ZnO particles in nano scale range. The most intense peak (101) is observed in all three methods. The XRD pattern exhibit single-phase polycrystalline nature of all the samples. All the peaks observe in the plot are found to be

in excellent agreement with the standard data from JCPDS-36-1451 [15]. From the XRD pattern peak intensity, position and width, Full width at Half maximum (FWHM) are calculated. The diffraction peaks located at 31.80°, 34.46°, 36.28°, 47.60°, 56.62°, 62.98°, 68.04°, 69.16° and 77.00° have been keenly indexed as hexagonal wurtzite single phase of ZnO in case of thermal decomposition. The crystallite size (D) of the prepared nanoparticles is determined by using Debye Scherrer's equation, $D = 0.9\lambda/\beta\cos\theta$, where λ is the wavelength of X-ray radiation, β is the full width at half maximum (FWHM), and θ is the diffracting angle. At θ diffracting angle the most intense peak is observed at (101) and $2\theta = 36.28$. The calculation of lattice parametes and crystalline size 'D' are presented in Table 1. It shows that the sample synthesized by the thermal decomposition method exhibits a higher crystallite size compared to the samples prepared by other methods.

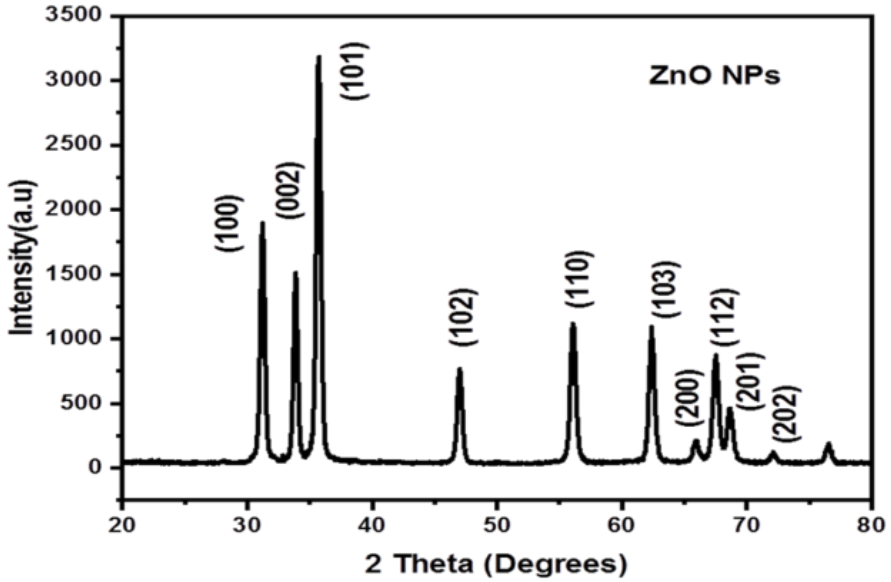

Figure 1. X-ray diffraction pattern of ZnO for Thermal decomposition.

Table 1. Variation in crystallite size and lattice parameters of ZnO sample

Sample	**Lattice Parameters a = b≠ c**	**Crystallite Size D (nm) D = 0.9λ/βCos θ**
ZnO (Sol-gel)	a = 3.24544 Å c = 5.20201 Å V =47.452 (Å)^3	26.62
ZnO (Hydrothermal)	a = 3.24980 Å c = 5.20491 Å V = 47.606 (Å)^3	38.592
ZnO (Thermal decomposition)	a = 3.29452 Å c = 5.29545Å V = 48.912 (Å)^3	42.48

Figure 2 displays the FTIR spectra of ZnO nanoparticles synthesized through the thermal decomposition method. An FTIR spectrum describes the various vibrational modes linked to the functional groups present in the sample, various absorption peaks are observed in this Figure 2. At around 3500 cm^{-1} indicates the existence of H_2O molecules on the surface of ZnO sample, which is associated with the O-H vibration. However, this peak is not observed in the FTIR spectrum of the other sample like sol-gel, suggesting the absence of water molecules on the surface of ZnO sample. At 2300 cm^{-1} the sharp peak observed in the FTIR spectrum corresponds to the presence of CO_2 molecules. Additionally, the absorption peak at 1500 cm^{-1} is attributed to the C=O bond, while the peak around 552 cm^{-1} is associated with the Zn-O vibration in stretching modes and it is present in all the three samples [16, 17].

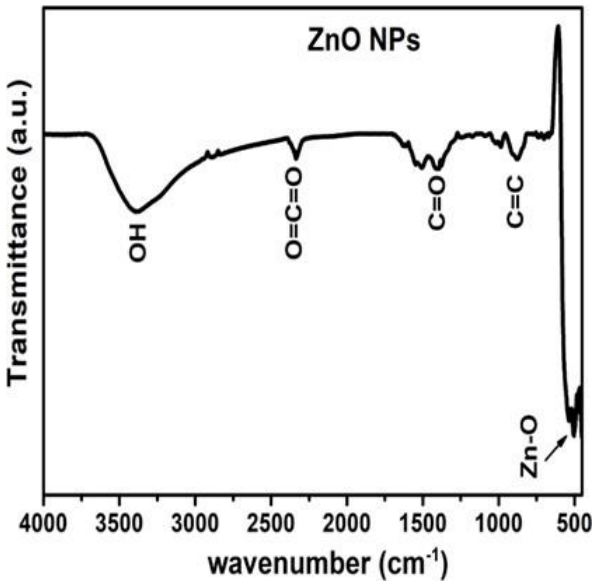

Figure 2. The FTIR spectra of ZnO NP's by thermal decomposition.

UV-visible spectra of the ZnO sample prepared by thermal decomposition shows an absorption peak around 376 nm as shown in Figure 3(a) whereas this peak has silently shifted in other samples prepared by other methods. This fact attributes the increase in crystalline size. Energy band gap of all the samples were calculated by Tauc's relation $Eg = \frac{1242.375(eV)}{\lambda}$[9, 10]. Figure 3(b) illustrates the plot of $(\alpha h\nu)^2$ vs photon energy ($h\nu$), an extrapolation of the linear region in the plot gives the value of the energy band gap. The calculated value of the energy band gap (Eg) are 2.78 eV for sol-gel combustion, 2.90 eV for thermal decomposition and 3.20 eV for hydrothermal synthesized sample respectively. It has been observed that the band gap (Eg) of hydrothermally synthesized ZnO NP's is found to increase. This increase in band gap can be attributed to defects associated with structural distortions within the material.

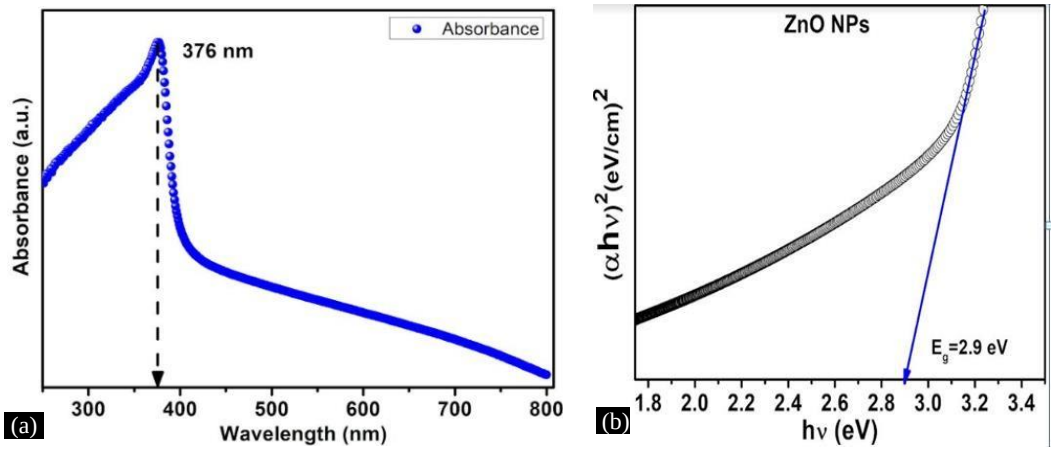

Figure 3. (a) UV-visible spectra of ZnO (b) the energy band gap (Eg).

Figure 4 (a) illustrates the surface morphology of ZnO nanoparticles prepared using thermal decomposition methods SEM (Model No. JSM 6510 LV, Make – JEOL, Japan) coupled with energy dispersive X-ray spectrometer (EDS), revealing the presence of a large number of spherical nanoparticles and rod-shaped nanostructures. In contrast, Figure 4 (b) showcases ZnO NP's prepared by thermal decomposition method, exhibiting a distinct wurtzite crystal structure. These results are reliable with the crystalline size obtained from the XRD patterns. Figure 4(c) shows the energy dispersive X-ray spectrometer (EDS) pattern of ZnO NP's.

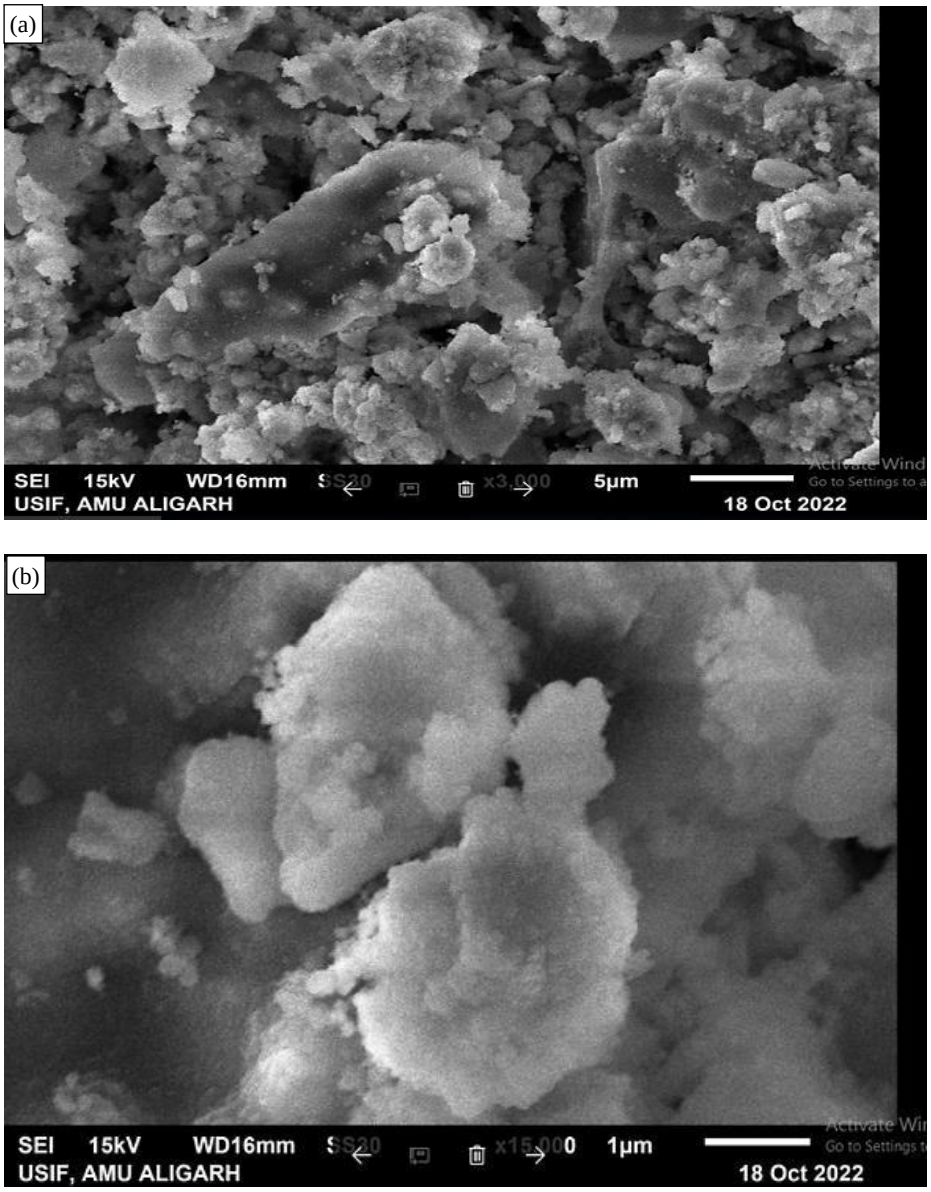

Figure 4. (a) SEM Images of ZnO NP's (b) wurtizite structure of ZnO NP's (c) EDS pattern of ZnO NP's.

CONCLUSION

Zinc oxide nanoparticles (ZnO NP's) samples are successfully prepared via three different ways, namely cost effective sol-gel, thermal decomposition and hydrothermal methods. Analysis of XRD patterns confirms the formation of all the samples in single phase and polycrystalline nature. The Rietveld refinement of the XRD data shows a hexagonal structure and its data is strongly matched with the standard data from JCPDS-36-1451. The average crystallite size is estimated by employing the Scherrer's equation and found to be approximately 27 nm, 39 nm and 42 nm for the sol-gel, thermal decomposition and hydrothermal synthesized samples respectively. SEM (Model No. JSM 6510 LV, Make – JEOL, Japan) images exhibit the formation of large spherical aggregated nanoparticles for Sol-gel method, wurtzite structure for thermal decomposition and also formation of Nano rods in hydrothermally synthesized ZnO sample, which can be confirmed further by using higher characterization technique i.e. Transmission Electron Microscopy (TEM). Energy dispersive X-ray (EDS) spectra ensure the purity and elemental composition in the samples. FTIR measurement confirms the ZnO stretching vibrational bands at ~552 cm^{-1}. The optical energy band gap (Eg) of the samples are calculated by Tauc's relation and found to be 2.9 eV in thermal decomposition method [18, 19].

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