



Facial Synthesis of Nano Sized ZnO by Hydrothermal Method

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ABSTRACT - In this contribution we are presenting a simple precipitation hydrothermal method to synthesize zinc oxide (ZnO) nanoparticles using zinc nitrate and starch solution. The obtained precipitated compound was calcined and structurally characterized by Powder X-ray diffraction (XRD), Scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR) and UV-Vis spectroscopic techniques. The powder X-ray data indicates that the calcined compound exhibits hexagonal (Wurtzite) structure with space group of P63mc (No. 186). Scanning electron micrographs show uniform spherical like morphology of ZnO. The SEM results reveal that the particle sizes were in the order of 30–50 nm and the average particle size is around 35 nm. The FT-IR result shows the existence of OH⁻, NO₂⁻, CO, CO₂ groups in unclaimed sample. The band gap was higher for synthesized ZnO particles than their bulk counterparts. The results indicate that starch is an attractive material that can be used as precipitation agent for preparing ZnO.

KEYWORDS - Zinc oxide, XRD, Nanostructure, Precipitation, starch

I. INTRODUCTION

ZnO is a unique and key inorganic material that has been attracted an extensive research due to its characteristic features and novel applications in wide areas of science and technology. It has multiple properties like semiconducting, piezoelectric, pyroelectric, catalysis, optoelectronics and powder metallurgy [1]. In addition, the optical properties of ZnO nanoparticles play a very important role in optoelectronic, catalytic and photochemical properties [2]. Recently, the material scientists all over the world have used different methods such as chemical vapor deposition (CVD), electro deposition (ED), hydrothermal, electrochemical, solution combustion, sol–gel, vapor–liquid–solid process, pulsed laser deposition and precipitation method for the preparation of ZnO powder and thin films with varied morphology and controlled growth which was stimulated because of strong dependency of its properties on size, shape and ratio of orientation [3-11].

ZnO is an intrinsic n-type semiconductor material that has been hexagonal structure with lattice parameters of $a=b=0.3250$ nm and $c=0.5207$ nm [12, 13]. Also, it has wide band gap of 3.37eV gives this material an upper hand compared to others [14, 15]. Due to these special criteria, the ZnO has an edge for applications of semiconductor including transparent electronics, ultraviolet (UV) light emitters, piezoelectric device, and chemical gas sensor, transistors, solar cells, catalysts and spin electronics [16-19]. Among all methods, precipitation and sol-gel technique provides suitable control of nucleation, ageing and growth of particles in solution. The direct precipitation is also one of the simple and cost effective methods for bulk production of materials [20]. In this method, particle growth owes to interact between different aqueous solutions and therefore very small particles are formed. Tiny size particles with lower solubility product dissolve and re-precipitate on the surface of larger particles in solution; consequently agglomeration takes place in solution as the particles clog together to minimize surface energy [21]. In this paper, a simple and cost effective direct precipitation method was used to synthesize ZnO nanoparticles using starch as a precipitating agent.

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II. EXPERIMENTAL

MATERIALS AND METHODS

A. Starting Materials and Synthesis of Zinc Oxide Nanoparticles

Zinc nitrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and soluble starch ($\text{C}_6\text{H}_{10}\text{O}_5$) were purchased from Fisher scientific, Germany and used without further purification. Distilled water was used to prepare precursor solution. ZnO nanoparticles were synthesized by hydrothermal method using zinc nitrate and starch as precursors. In a typical synthesis, 1.3 gm soluble starch dissolve in 200 ml DI water after that placed in the oven for 15-20 mins, when starch is completely dissolve in water, 7.5gm zinc nitrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) added it was kept under constant stirring for 1 hour. In the same way 1.7 gm NaOH was also prepared in 150 ml of distilled water. The NaOH solution added dropwise in the zinc nitrate and starch solution with vigorous stirring [22]. The final precipitating solution was centrifuged at 6000 rpm for 8 min and washed with acetone to remove any impurities or possible absorbed ions. The chemical reactions occurred in this process is shown in fig.1

B. Structural Characterization - To determine the crystal phase identification and estimate the crystallite size, powder X-ray diffraction (XRD) patterns were recorded for synthesized samples using Bruker - D8 Advance Powder X-ray diffractometer with $\text{Cu K}\alpha$ radiation, ($\lambda_{\text{Cu}} = 1.5418 \text{ \AA}$) working at 30 mA and 40 kV. To measure the particle size and morphology of ZnO nanoparticles, LEO-Libra 120 and scanning electron microscopy (SEM), Zeiss Supra 35VP were used. Fourier transform infrared spectra (FT-IR) were obtained on KBr pellets at ambient temperature using a Bruker FT-IR spectrometer (TENSOR 27). FT-IR spectroscopy in the transmission mode gives qualitative information about the way in which the adsorbed molecules are bonded to the surfaces as well as the structural information of solids. The UV-Vis absorption spectra were recorded by Mettler Toledo spectrophotometer. The nanoparticles were dispersed in ethanol and were sonicated prior to UV-Vis measurement for uniform dispersion.

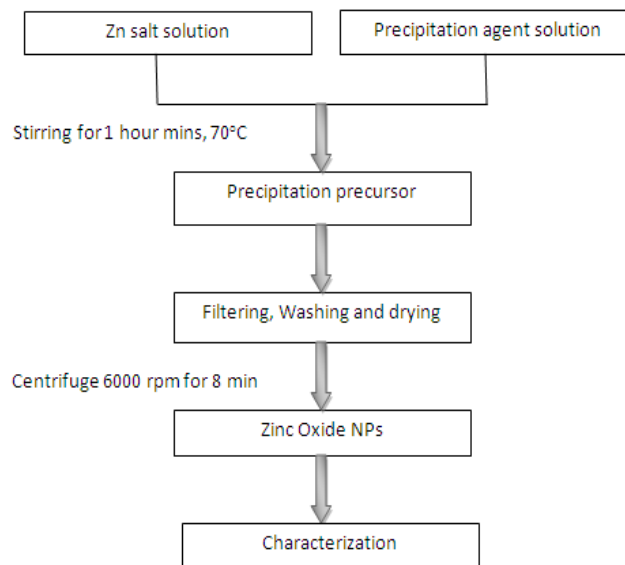


Fig.1: Chemical reactions to synthesize zinc oxide nanostructure

III. RESULTS AND DISCUSSION

a. Powder X-ray diffraction (XRD) studies

The XRD peaks in the wide angle range of 2θ from 10° to 90° with $\text{CuK}\alpha$ radiation. It can be seen from Fig.2, the powder XRD patterns were indexed to pure hexagonal structure with lattice parameter of $a = 3.25 \text{ \AA}$ and $c = 5.2 \text{ \AA}$ and

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its space group: P63mc. The peaks appeared at 2θ range of 31.76° , 34.42° , 36.25° , 47.53° , 56.59° , 62.86° , 66.37° , 67.94° , 69.08° , 72.56° , 76.95° values corresponds to pure ZnO. They are matching with the standard JCPDS card no. 01- 79-0206, indicating that the ZnO particles are crystalline structure. The average crystallite sizes were calculated by using the Debye - Scherer equation:

$$D = K\lambda / \beta \cos\theta$$

where D is the diameter of the crystallite size, K is the shape factor (the typical value is 0.9) λ is the wavelength of incident beam, β is the broadening of the diffraction line measured in radians at half of its maximum intensity (FWHM) and θ is the Bragg's angle [23]. From the XRD data, the average crystallite sizes were found to be 35 nm. No other peaks were observed in calcined compound, which indicates the formation of a pure hexagonal structure of ZnO. Fig 2. shows X-ray diffraction patterns of zinc oxide nanoparticles.

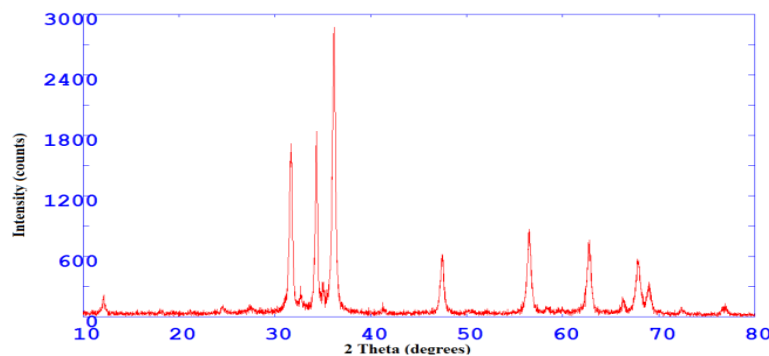


Fig 2. X-ray diffraction patterns of zinc oxide nanoparticles

b. SEM analysis

Fig.3 reveals the SEM images of ZnO nanoparticles and we observed the particles were well defined and small spherical shaped with agglomerated particles. It can be observed that ZnO nanoparticles mainly present granules with small spherical shape and are well crystallized.

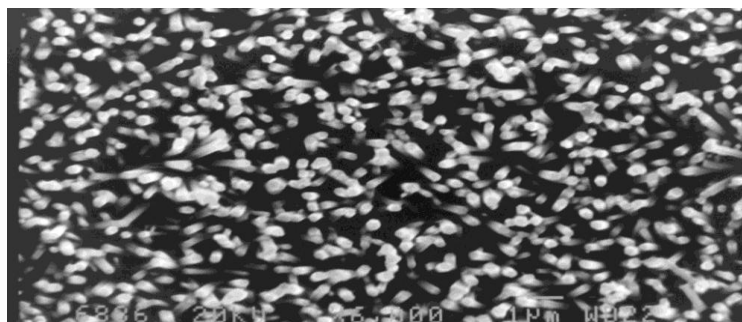


Fig 3. SEM image of ZnO nanoparticles

c. FT-IR Spectroscopy

Infrared spectroscopy was used to detect the presence of functional groups adsorbed on the surface of synthesized nanoparticles during precipitation process indicates that the absorption peak in the range of $3200\text{--}3600\text{ cm}^{-1}$ was observed. This was centered at 3430 cm^{-1} corresponds to the stretching vibration of intermolecular hydrogen bond (O–H) existing between the adsorbed water molecules and indicates the higher amount of hydroxyl group.

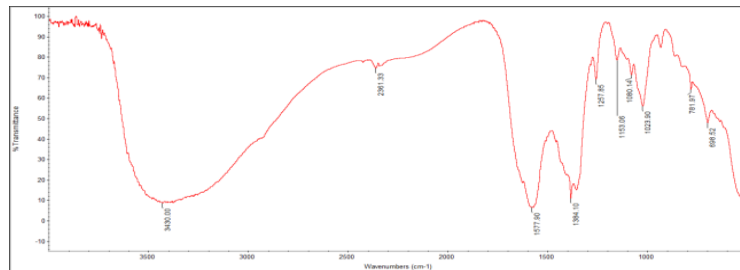


Fig.4. FT-IR spectra of ZnO

The results were well matched with the observation done by Xian et al. [24]. The peaks at 1384.10 and 1577.90 cm^{-1} are attached to ZnCO_3 and bending vibrations of $\text{Zn}(\text{OH})_2$, and the absorption band in 600–1100 cm^{-1} is due to the lattice vibration of CO_3^{2-} . It is interesting to note the two weak bands at 2920 cm^{-1} in calcined compound corresponding to the C–H stretching, which indicates that its molecules were present on the surface of ZnO nanoparticles. The band near at 2361.33 cm^{-1} confirms the presence of bending vibrations of the intercalated O=C=O species produced by the starch decomposition in the initial process of preparation. The weak band at 698.52 cm^{-1} and 781.97 cm^{-1} . This indicates the presence of ZnO nanoparticles.

d. UV–Vis spectroscopy

For recording UV–Vis spectra, the sample of ZnO solution was prepared by ultrasonically dispersing them in absolute ethanol. The absorption peak in Fig.5 correspond to ZnO sample calcined at a temperature of 500 °C showing the strong absorption in the wavelength of 280 nm. This can be assigned to the intrinsic band gap absorption of ZnO due to the electron transitions from the valence band to the conduction band [6]. The band gap (E_g) of ZnO nanoparticles was calculated by using the formula $E_g = hc/\lambda$ [25], where h = Planck’s constant, c = velocity of light and λ = wavelength.

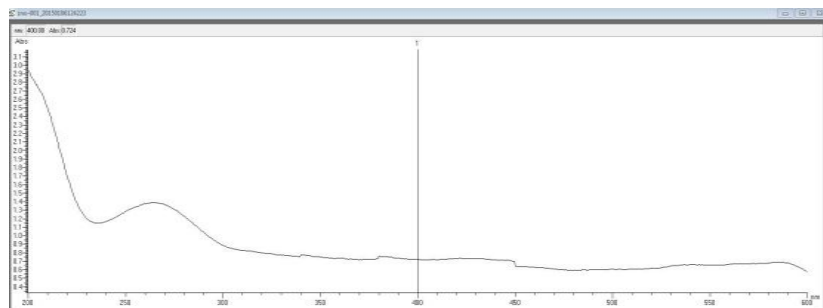


Fig 5. UV–Vis spectra of ZnO

IV. CONCLUSION

In the present work, the nanosized ZnO particles were successfully generated by hydrothermal method using zinc nitrate as zinc source and starch solution as precipitating agent in aqueous solution. In XRD analysis, the size range of the generated ZnO powder was approximately 30–50 nm. The SEM analysis shows that the particles morphology was spherical structure. The FT-IR spectrum shows the existence of OH-, CO₂, NO₂ and CO groups in unclaimed sample. The band gap was lower for synthesized ZnO nanoparticles than their bulk counterparts. Thus, the synthesis of ZnO nanoparticles by direct precipitation method is simple, fast and eco-friendly in nature. These nanoparticles may be used as a reference electrode fabrication for sensing/detection applications.



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