SYNTHESIS, CHARACTERIZATION AND DFT STUDIES OF ZNO NANOPARTICLES BY USING CO-PRECIPITATION METHOD

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Abstract

In this study, we confidently employed the co-precipitation method to successfully produce nano-sized ZnO powder. The starting materials are Zinc Sulphate and Sodium Hydroxide in aqueous solution. The precipitated compound was calcined and characterized by using UV-Visible spectroscopy, SEM, EDX, and FT-IR spectral data. The DFT studies were also done by these ZnO nanomaterials.

Keywords: ZnO, nanomaterials, co-precipitation method, Characterization, DFT studies.

Introduction

The regulation of size, shape, and composition is a crucial aspect of nanomaterial synthesis. These parameters have a significant impact on the properties of nanomaterials, thereby determining their diverse technological applications[1,2]. Due to its exceptional physical and chemical properties, zinc oxide is a versatile material with high chemical stability, a wide range of radiation absorption, high photostability, and a high electrochemical coupling coefficient[3,4]. Various methods have been used to synthesize ZnO nanomaterials. The key to utilizing ZnO nanomaterials for different applications lies in controlling their physical and chemical properties, including size, shape, surface state, crystal structure, organization on a support, and dispensability[5,6]. There have been numerous techniques developed for synthesizing nano compounds. For instance, Hong et al. employed a controlled precipitation method to achieve a single-step process with large-scale production. The essential advantage of this method is that it avoids unwanted impurities, making it a cost-effective way to prepare ZnO nanoparticles[7].

The precipitation method was used to obtain nano-sized zinc oxide from aqueous solutions, with an attempt to modify the micro-emulsion process for achieving mono-dispersed zinc oxide[8]. A study conducted by Kang et al. focused on the continuous synthesis of zinc oxide nanoparticles in a microfluidic system for potential use in photovoltaic applications. Their research involved a combination of numerical simulations and experimental methods to investigate the synthesis and characterization of ZnO nanoparticles[9].

Materials and Methods

Materials: ZnSo4 (Zinc Sulphate), NaOH (Sodium Hydroxide), Dil.Water, Magnetic stirrer, Muffle furnace, Hot air oven.

Method: Co-Precipitation Method.

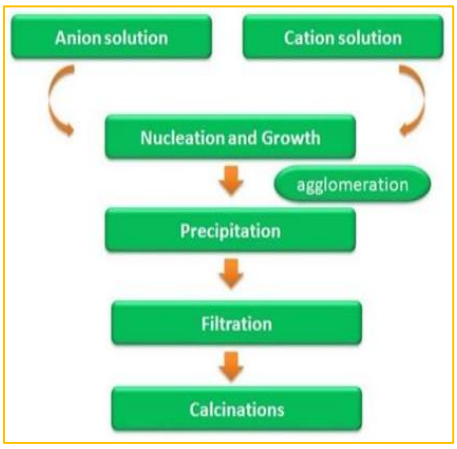


Figure 1: Precipitation Method

Synthesis of ZnO nanoparticles

Add the sodium hydroxide solution drop by drop to the zinc sulfate solution while stirring vigorously, using a ratio of 1:2 molar concentration.

Figure 2: ZnSo4 & NaoH

The stirring continued for 12 hours

Figure 3: Stirring

The precipitate obtained is filtered and washed thoroughly with deionized water.

Figure 4: Filtration and White Precipitate

The precipitate is dried in an oven at 100^0C and ground to a fine powder using agate mortar.

Figure 5: Dried Precipitate

The powder obtained from the above method is calcinated at different temperatures suchas 300^0C, 500^0C, 700^0C, and 900^0C, for 2 hours.

Figure 6: Calcination Process

Step-by-step process of ZnO nanoparticles preparation

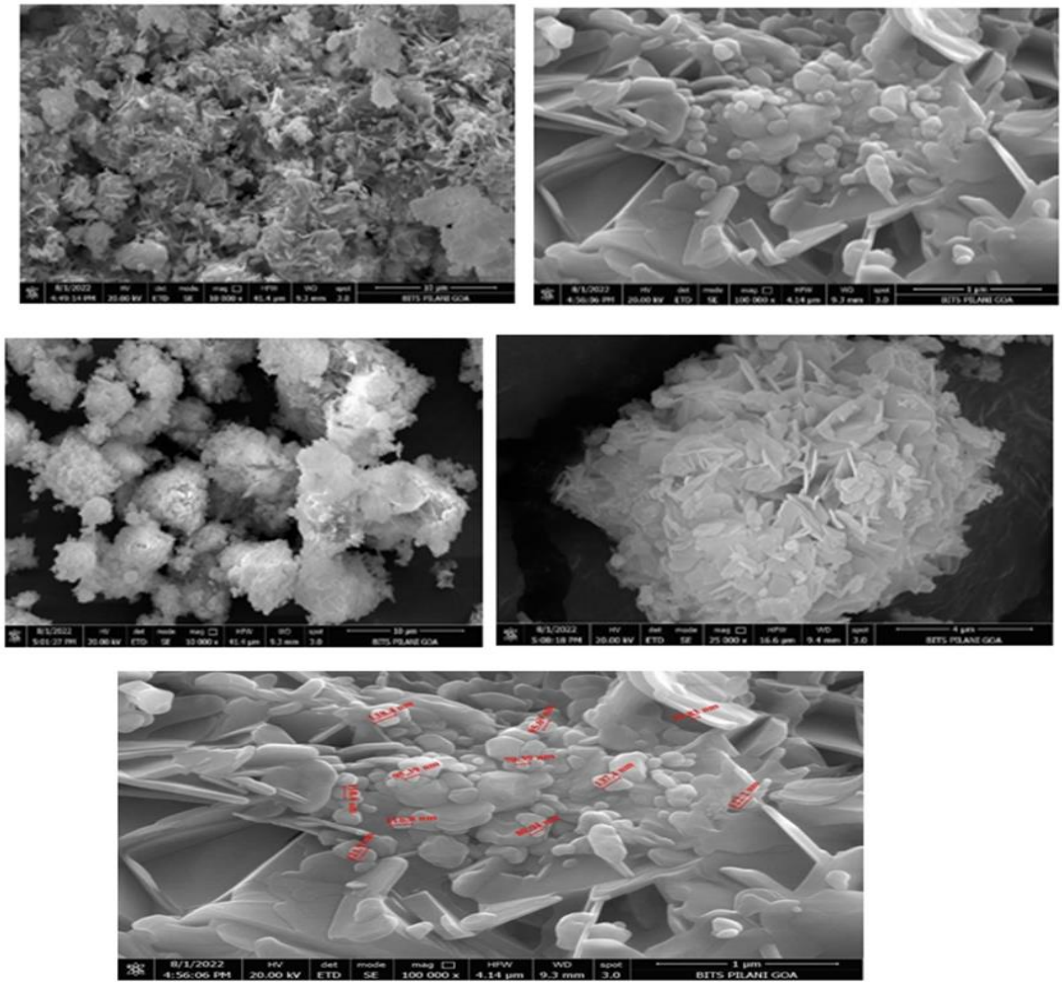
- ✓ 28.7 gm of ZnsO4 and 8gm 0f NaOH dissolved in distilled water separately.
- ✓ Two solutions are mixed in a beaker placed under continuous stirring on the magnetic stirrer.
- ✓ Stirring is continued for 12 hours.
- ✓ Calcinated at different temperatures 300^0C, 500^0C,700^0C, 900^0C for 2hrs.
- ✓ Continuously stir until a white precipitate is formed. it is filtered and washed with deionized water.
- ✓ Placed in an oven at 100^0C until the solvent is evaporated.

Results and Discussions

The nano-size ZnO powder was prepared by using Zinc Sulphate (ZnSo4) and Sodium hydroxide (NaOH) by using the precipitation method. Here ZnO powder was investigated by 5 different analyses. The SEM, EDX, XRD, UV, and FTIR analyses have shown clear results.

SEM Analysis

The surface morphology of pure ZnO nanoparticles was examined using FE-SEM, despite their non-uniformity. The results show that the ZnO NPs developed at different calcination temperatures are in the nano range and have flake-like shapes, as seen in the typical SEM images and the corresponding particle size distribution. The ZnO NPs obtained at different temperatures (300°C, 500°C, 700°C, and 900°C) had average diameters of 39.83 nm, 79.39 nm, 80.94 nm, and 95.39 nm, respectively. As the calcination temperature increased, the particle size also increased. The SEM images were used to measure the size of each particle separated and calculate the distribution of particles in the samples. The average size was then plotted and shown in the figures.



Figures 7: FESEM Result in different calcination (300^0C, 500^0C, 700^0C, 900^0C)

Energy-Dispersive X-Ray Spectroscopy (EDX)

The purity of Zno NPs can be accurately determined through EDX analysis. This method helps to identify the element composition present in the samples. Based on the results, it was found that the EDX data consisted of two primary elements, namely Zn (80.3%) and O (19.7%). This confirms that the Zno NPS is of high purity. This finding is consistent with similar studies conducted by Brintha and Ajith, where the mass percentage of Zn and O were also found to be 80.3% and 19.7%, respectively. Therefore, the EDX results confirm that the synthesized ZnO NPs are of high purity and contain a high level of Zn and O element composition.

Table 1: **EDX Analysis**

Element	Weight %	Atomic %	Net Int	Error %	K ratio	Z	A	F
Zn	80.3	50.0	752.7	2.5	0.6417	0.9319	1.0036	1.0025
Oxygen	19.7	50.0	0.0	0.0	0.0000	0.0000	0.0000	0.0000

X-ray Diffraction Analysis

The XRD analysis provides a comprehensive understanding of the crystal phases and crystallinity of the ZnO that was prepared. The X-ray diffraction pattern of ZnO NPs, which were subjected to varying calcinated temperatures, revealed nine main broad bands at 2θ values of 31.77^{o}, 34.44^{o}, 36.26^{o}, 47.53^{o}, 56.56^{o}, 62.63^{o}, 67.93^{o}, and 67.8^{o}, corresponding to crystal structures of (100), (002), (101), (102), (110), (103), (200), and (112), respectively. The Debye-Scherrer equation was utilized for calculating the average crystallite sizes of the samples. Applying the equation $D = 0.9\lambda/\beta \cos(\Theta)$, where D is the crystallite size in nanometers, λ is the wavelength of the X-ray in nanometers, β is the full width at half maximum, and θ is the diffraction angle, revealed that the average crystalline size increased with higher calcinated temperatures, up to a range of 30 nm.

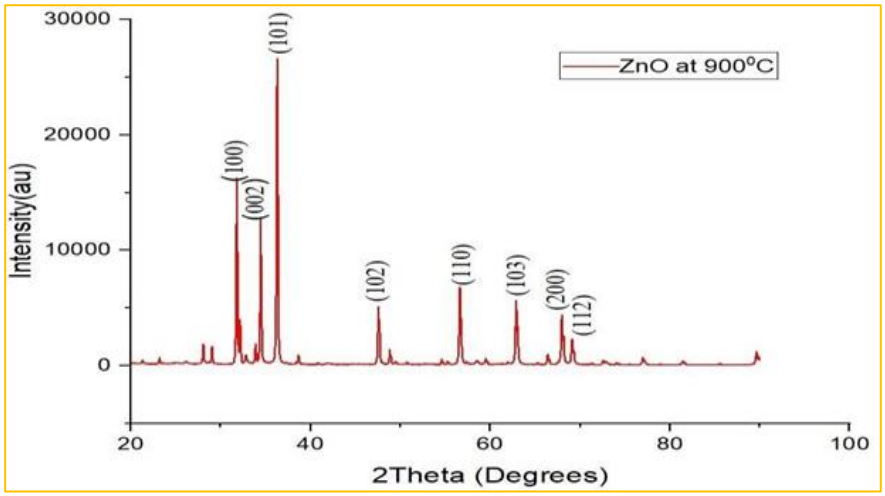


Figure 8: XRD calcinated at 900^{0}C

FT-IR spectra

The functional groups of synthesized ZnO NPs were explained through the FT-IR spectrum. The spectrum displayed a broad absorption band at 414 cm^{-1}, which can be attributed to Zn-O

stretching vibration. Although various synthetic methods have been used to create ZnO NPs, the FT-IR spectrum obtained from their synthesis showed similarities.

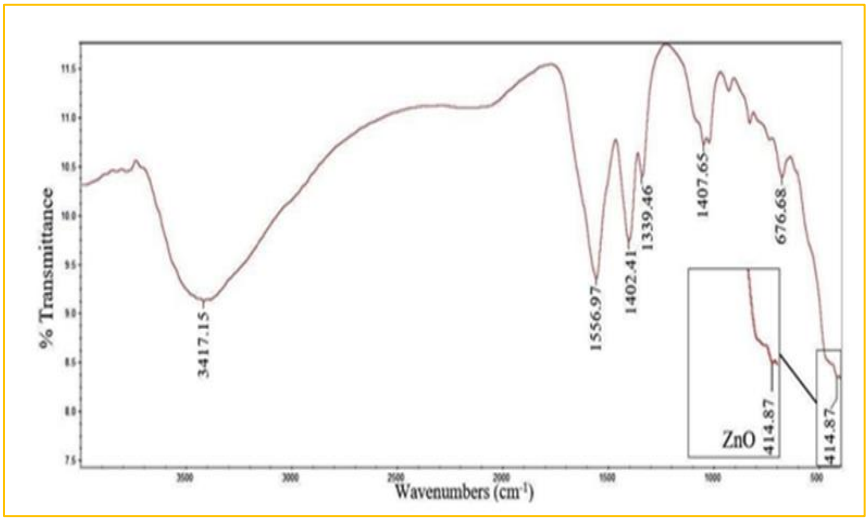


Figure 9: FT-IR spectrum of synthesized ZnO NPs

UV-Vis spectra

The formation of ZnO nanoparticles was confirmed through UV-vis spectra analysis. All of the samples exhibited a prominent maximum absorption level below 400 nm. The optical absorption of ZnO nanopowders, which were calcinated at varying temperatures ranging from 3000 K to 9000 K, displayed strong absorption peaks at 384.6 nm, 381 nm, 384 nm, 383.5 nm, and 382.5 nm, respectively. The results indicated that an increase in the calcination temperature of ZnO samples caused a shift towards a lower wavelength, with the exception of the sample at 9000 K.

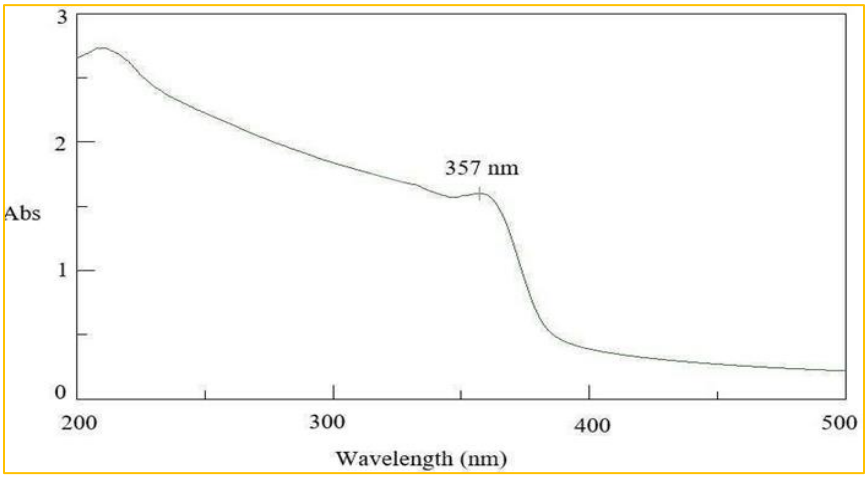


Figure 10: UV spectrum of synthesized ZnO NPs

DFT studies

DFT Computational studies have been performed using ABINIT software. The primitive cell of ZnO (1010) surface and Energy optimized structure were studied.

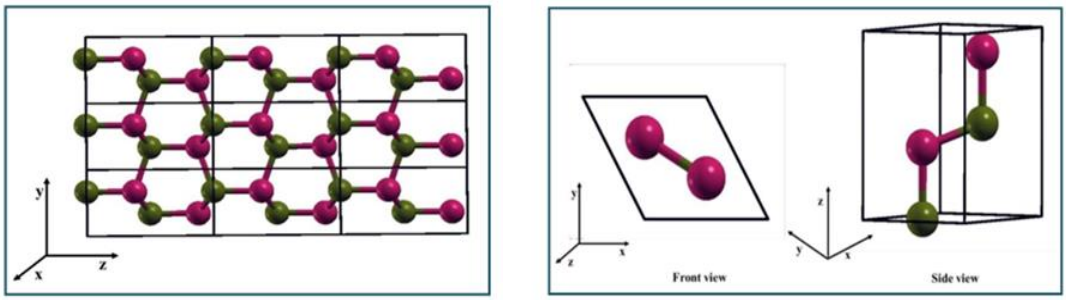


Figure 11: Side view of a supercell of ZnO primitive unit cell and Energy optimized structure of ZnO (1010) surface (a) front view, (b) side view

By using ABINIT software the band gaps were observed for nano and bulk structures of ZnO. For bulk observation, EG (Direct) = 0.451eV and Nano EG(Direct) = 0.59eV.

When particles reach the nanoscale, there is a decrease in the overlap of orbitals or energy levels. As a result, the energy band gap between the valence band and the conduction band becomes thinner, causing an increase in energy levels. This phenomenon can be explained through quantum mechanics.

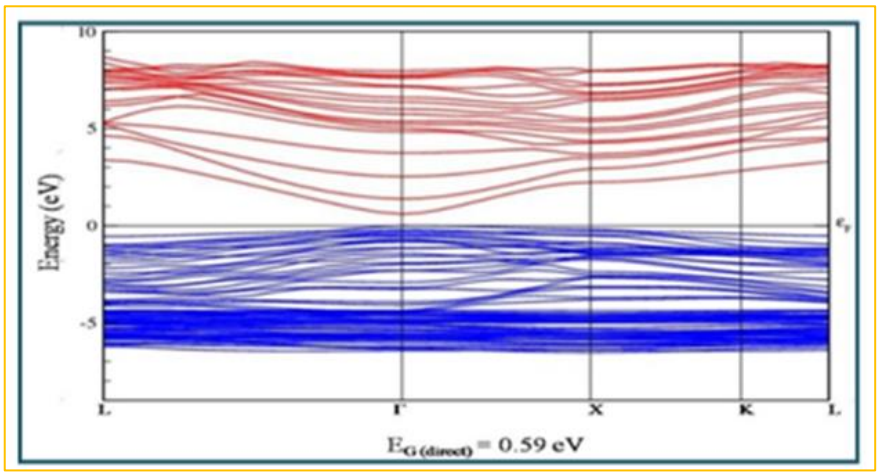


Figure 12: Electronic band structure of Nano ZnO (1010) surface

Conclusion

Zinc Oxide Nano-powder was synthesized with ease and success using the co-precipitation method. The ZnO NPs obtained with different calcinated temperatures (300^0C, 500^0C,700^0C, and 900^0C) showed average diameters of NPs 39.83, 79.39, 80.94, and 95.39 nm. It confirmed the particle size increases with increasing the calcinated temperature.

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