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Characterization of Engineered Zinc Oxide (ZnO) Nanoparticles Using Different Techniques

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Abstract

The characterization of chemically fabricated zinc oxide (ZnO) nanoparticles, involved the utilization of diverse techniques for characterization. The utilization of X-ray diffraction (XRD), *scanning electron microscope* (SEM), Transmission Electron Microscopy (TEM) and *Fourier-transform infrared spectroscopy (FTIR)* (FTIR) in the assessment of zinc nanoparticles unveiled their crystalline structure and high purity. Results exhibited that ZnO nanoparticles had a flattened spherical morphology with a textured surface, demonstrating an average size spanning from 80 to 130 nm and well-organized with minimal aggregation was observed using SEM imaging. The TEM analysis corroborated the particle size determined through XRD, indicating a dimension of around 65 nm. Notably, FTIR analysis unveiled discernible peaks, with a specific narrow band observed at 3450 cm^{-1}, confirming the presence of Zn-O bonds. These findings indicate that engineered ZnO particles were confined to the nano range, which has potential application in agricultural fields as nutrient carriers.

Keywords: ZnO nanoparticles, Electron Microscopy, X-Ray Diffraction

Introduction

Nanotechnology, at the forefront of science and technology, arises from the convergence of various fields of study, leading to a domain of unprecedented advancement. In the agriculture and fertilizer sector, the use of nanotechnology-enabled nano nutrients has emerged as the main key player in different avenues of this industry *i.e.,* nano-fertilizers (enhancing nutrient use efficiency), new-generation pesticides and reclamation of salt-affected soils (DeRosa *et al*., 2010). Particles with one or more dimensions in the ≤ 100 nm or less range are referred to as nanoparticles (Huber, 2005). Nanoparticles possess unique properties such as small size and high specific surface area, which enhance their reactivity (Liscano *et al*., 2000; Milani *et al*., 2015) and due to this, these nanoparticles may act as ideal materials for efficient fertilizer use (Joseph and Morrison, 2006). Zinc oxide, in particular, is considered a promising and practical approach to environmental protection and the second most abundant metal oxide after iron, is cost-effective, safe, and easily prepared (Kalpana *et al*., 2018). The ZnO isomer is called a wurtzite-type and it is FDA-approved and can solubilize in acidic environments, making them promising nanocarriers for drug delivery (Gobinath *et al*., 2021; Lakshmipriya and Gopinath, 2021). ZnO nanoparticles were successfully synthesized using various methods, including the sol-gel approach, precipitation method, green leaf extract method, microwave method, wet chemical method, and hydrothermal method. Nano-sized zinc oxide was synthesized using various precursors and alkalis like acetate-based zinc salts with NaOH and

Oxalic acid as reactants, respectively (Rajendran *et al*., 2022). The prepared materials were studied by measuring the size, shape, and morphology under X-ray diffraction, Scanning electron microscopy, and Transmission electron microscopy. Crystalline oxide powders offer chances for acquiring better chemical, mechanical, optical, or electrical properties when mixed with other materials (Gobinath, R *et al*., 2015; Manjunatha *et al*., 2019). In the present investigation, we have characterized the ZnO nanoparticles for their size, shape, and composition using various techniques for their use in agricultural fields. We have employed different techniques namely, X-ray Diffraction, Scanning electron microscopy, Transmission electron microscopy and Fourier transmission infra-red (FTIR) for confirming the characteristics of engineered ZnO nanoparticles.

Materials and Methods

Characterization of ZnO nanoparticles

The Zinc Oxide nanoparticles (analytically pure) were purchased from Sigma-Aldrich (Germany) and characterized using techniques like XRD, SEM, TEM, and FTIR for their size, shape and crystallinity.

X-ray diffraction (XRD)

X-ray diffraction, also known as XRD, is a scientific technique used to analyze the structure of materials. The crystallite and purity of ZnO nanoparticles are identified and determined by the XRD pattern by using the X-ray diffraction technique using Philips PW 1710 X-ray diffractometer. For this purpose, automated powder diffraction (APD) software with Cu kα radiation (λ=1.5418 Å) source was used. An operating system with a power of 15 kV and Kβ filter was used as a background filter. A powdered nanoparticle is placed in a sample holder and the sample was scanned at a diffraction angle of 2θ from 3 to 50°. The average particle diameter D of the nanoparticle is determined with the help of main peaks obtained from the XRD image; using Debye-Scherer's formula as follows:

$$D = k\lambda/(\beta\cos\theta)$$

Here λ is the x-ray wavelength (Cu kα = 1.5418 Å)

k is the machine constant (0.916)

β is the full width at half maximum (FHWM) of the peak and θ is the peak position.

Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) is used to reveal information about the sample including external morphology (texture), composition, and structure. Morphology and surface modification of synthesized nanoparticles were determined by EVO/MA10 scanning electron microscopy (SEM) of CARL Zeiss instrument equipment. ZnO nanopowder is trapped on double-sided sticky carbon tape covered copper stab and coated with a palladium layer in a vacuum of 10-3 torr for a minimum of 6 hours to fixation.

Transmission electron microscopy (TEM)

Powdered nanoparticles were made into suspension placed on the grid, dried under a vacuum, and then placed on the grid plate to reduce the settlement of the nanoparticles. Suspension mounted grid was kept under an infra-red lamp for one hour for fixation and then analyzed under Joel JEM 1010, USA. Images were captured by Olympus digital camera and analyzed with the help of installed software.

Fourier transmission infrared spectroscopy (FTIR)

Functional groups present in the compounds were analyzed by Fourier transmission infrared spectrometer. The analysis is carried out using the principle of vibrational a stretching motion of atoms or molecules. These compounds absorb electromagnetic energy in the infrared region of the spectrum. The position of a particular absorption band is specified by a particular wave number. The powdered sample is analyzed in the Brucker: ALPHA, FTIR, ATR system (Typically 24 scans, Resolution- 4cm^{-1}) with scanning between 4000-400 cm^{-1}.

Results and Discussion

X-ray diffraction (XRD)

The crystallite size and purity of the synthesized ZnO nanoparticle were determined by X-ray diffraction (XRD), where the X-ray diffraction patterns were as follows; diffraction angles (2θ) of 31, 34 and 35, and the peak list was given in **(Table 1)**. These peaks corresponded to the crystal planes of the ZnO structure, specifically the 100, 002 and 101 planes (**Figure 1**), with no impurity peaks. The Debye-Sherrer equation was used to calculate the particle size using with diffraction angle of the intense peak. Additionally, these peaks align with the standard wurtzite structure observed in the powder diffraction standard image of JCPDS card no. 36-1451 (Morkoc and Ozgur, 2008; Gobinath *et al.*, 2021). A similar result was recorded by Alwan *et al.*, (2015) in which ZnO nanoparticles produced using the sol-gel method exhibited platy structure orientation and an intense peak was observed at 58.3 nm from the width of dominant peaks (100) and (101) reflections according to the Debye - Scherrer equation. Furthermore, utilizing the Debye-Sherrer equation, the average size of the ZnO nanoparticles was determined to be 45-60 nm.

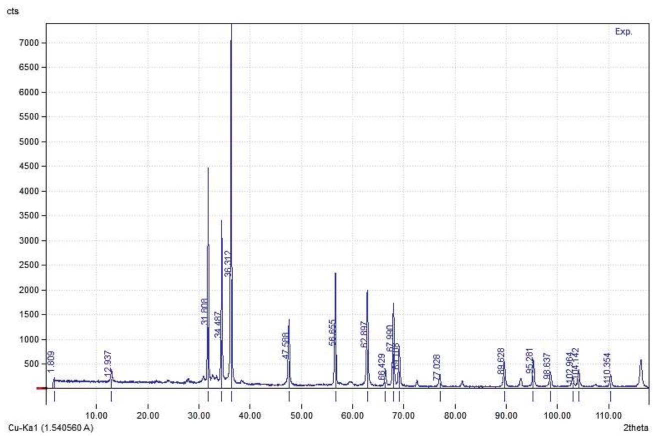


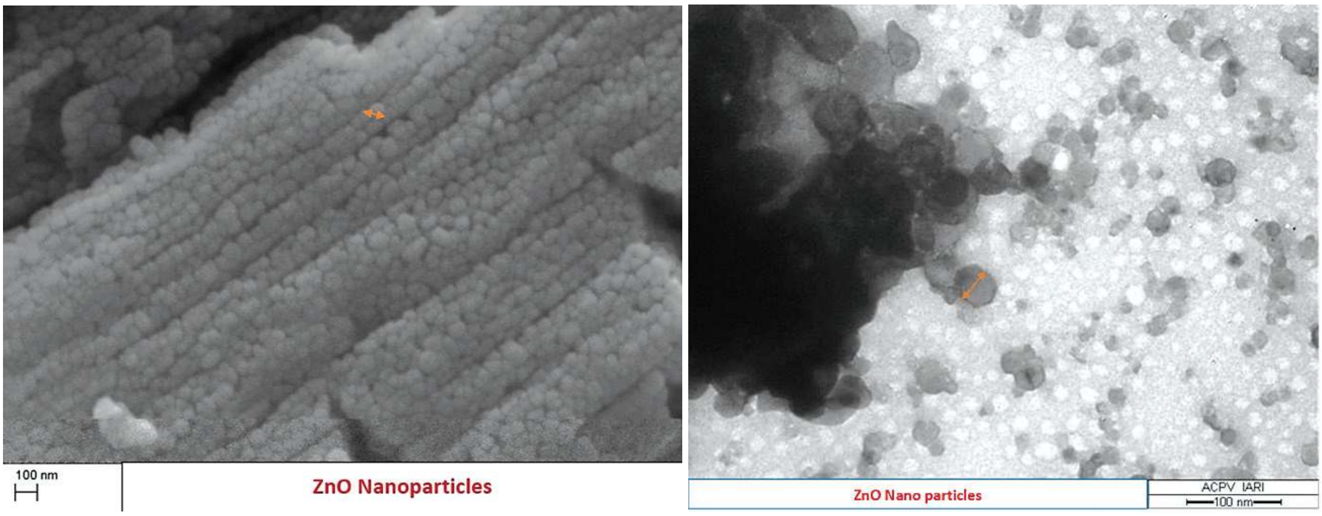
Figure 1: X-Ray Diffraction pattern

Table 1: Phase analysis report on XRD peaks-ZnO nanoparticles

No.	2θ [°]	D [Å]	I/10 (Peak height)	Counts (Peak area)	Full Width Half Maxima (FHWM)
1	1.81	48.8085	21.45	221.43	1.0641
2	12.94	6.8375	37.50	181.81	0.4998
3	31.81	2.8110	604.39	1242.62	0.2120
4	34.49	2.5985	447.81	975.63	0.2246
5	36.31	2.4720	1000.00	2199.12	0.2267
6	47.59	1.9092	183.60	546.32	0.3068
7	56.66	1.6233	318.54	812.23	0.2629
8	62.90	1.4764	264.66	786.35	0.3063
9	66.43	1.4062	45.97	130.37	0.2924
10	67.99	1.3777	235.66	689.05	0.3015
11	69.11	1.3581	110.10	331.27	0.3102
12	77.03	1.2370	30.08	105.49	0.3616
13	89.63	1.0929	68.27	242.89	0.3668
14	95.28	1.0424	72.88	260.01	0.3678
15	98.64	1.0157	39.49	141.30	0.3689
16	102.96	0.9845	23.72	108.37	0.4710
17	104.14	0.9766	45.28	180.79	0.4116
18	110.35	0.9383	31.64	111.67	0.3638

Scanning electron microscopy (SEM)

The scanning electron micrographs were utilized to analyze the morphology and size of the nanoparticles, revealing distinct characteristics of the ZnO nanoparticles. Notably, ZnO nanoparticles showcased an average size falling within the range of 60-130 nm (**Figure 2**). Further examination revealed that the ZnO nanoparticles possessed a well-ordered structure with moderate to less aggregation induced by physical forces. The results indicated that these nanoparticles were in irregular shapes and sizes due to moderate aggregation. According to Alwan *et al*., (2015) and Manjunatha *et al*., (2019) in which ZnO nanoparticles produced using a sol-gel method and hydrothermal process were spherical and changed to flower-like arrangement.



(a) **(b)**

Figure 2: Image of a) Scanning electron microscope and b) Transmission electron microscope (TEM) image

Transmission electron microscope (TEM)

The transmission electron microscopy images of the ZnO nanoparticles provided a detailed depiction and the size is determined as 45 nm. These TEM images provided conclusive evidence regarding the dimensions and shape of zinc nanoparticles (**Figure 2**). The ZnO nanoparticle exhibited a crystalline nature, with an average particle size of approximately 90 nm. The particles displayed a smooth and spherical morphology, which aligns with the previous findings by Dakhlaoui *et al*., (2009). This observation indicates that the particle morphology is predominantly spherical and uniform, though it is partly aggregated due to strong physical forces between individual particles. A similar result was found by Rajakumar *et al*., (2018) in which ZnO nanoparticles produced were spherical and hexagonal geometries.

Fourier-transmission infrared spectrophotometer (FTIR)

The chemically synthesized zinc oxide (ZnO) nanoparticle underwent Fourier-transform infrared (FTIR) analysis, and the resulting spectral band was presented in **(Figure 3)**. The spectral image of the ZnO nanoparticle featuring distinct peaks at the following wavelengths 486, 1626, and 3450 cm^{-1}, respectively. The FTIR spectrogram revealed a stretching peak at 486 cm^{-1} (Zn-O bonds) and other vibrational stretches was observed at 2456 (O-H bond) and 3450 cm^{-1} (C=O bond) in small amounts, likely originating from atmospheric moisture and carbon dioxide (CO_2) absorption (Gobinath *et al*., 2021; Hasindawani *et al*., 2016; Xiong *et al*., 2006; Parthasarathi and Thilagavathi, 2011). Based on the results, it can be concluded that the precursor used in the synthesis did not significantly alter the functional composition of the ZnO nanoparticles. A similar result was observed by Kumar and Rani (2013) that the FT-IR spectra confirmed the existence of Zn-O bonding and the adsorption of surfactant molecules onto the surface of ZnO nanoparticles.

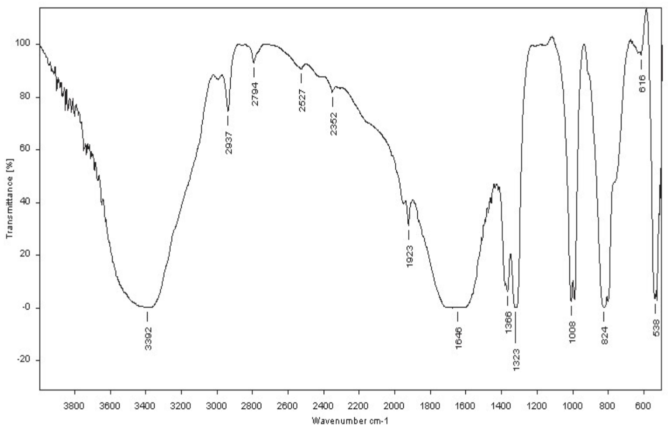


Figure 3: Fourier Transmission Infra-red spectroscopy (FTIR) image

Conclusion

In the present study, XRD analysis revealed the phase purity of engineered ZnO nanoparticles and crystalline in nature. The SEM and TEM analysis revealed a flattened spherical nanoparticle with a rough surface texture. The FTIR pattern analysis exhibited distinct peaks, stretching with the narrow band confirming the presence of Zn-O bonds. However, further investigation like the use of BET and DLS techniques is required for a better delineation and understanding of the properties of ZnO particles. Based on the results, these ZnO nanoparticles can be used in a variety of fields like agriculture as nutrient supplements, solar cells, antifungal, antibacterial material and targeted delivery of nutrients in biomedical fields.

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