

Phytochemical-Assisted Low-Temperature Hydrothermal Crystallization of Defect-Engineered ZnO Nanoparticles Using *Madhuca longifolia* Flower Extract: Structural Evolution and Tunable Optical Properties

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Research Article

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Posted Date: September 16th, 2026

DOI: <https://doi.org/10.21203/rs.3.rs-10663727/v1>

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Additional Declarations: No competing interests reported.

Phytochemical-Assisted Low-Temperature Hydrothermal Crystallization of Defect-Engineered ZnO Nanoparticles Using *Madhuca longifolia* Flower Extract: Structural Evolution and Tunable Optical Properties

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Abstract

Zinc oxide (ZnO) nanoparticles are promising wide-band-gap semiconductors owing to their excellent optical properties, high exciton binding energy, and chemical stability. However, synthesizing phase-pure, highly crystalline ZnO at low hydrothermal temperatures without post-synthesis calcination remains challenging. Herein, a phytochemical-assisted hydrothermal method employing *Madhuca longifolia* (Mahua) flower extract as a natural reducing and capping agent was developed to synthesize defect-engineered ZnO nanoparticles at 80–100 °C. The green approach enabled the direct formation of phase-pure hexagonal wurtzite ZnO without calcination. X-ray diffraction revealed enhanced crystallinity with increasing hydrothermal temperature, evidenced by crystallite growth from 24.9 to 36.7 nm and reductions in microstrain (4.67×10^{-3} to 3.19×10^{-3}) and dislocation density (1.61×10^{-3} to $7.43 \times 10^{-4} \text{ nm}^{-2}$). X-ray photoelectron spectroscopy showed a decrease in oxygen-vacancy concentration from 26.8% to 13.5%, while Raman spectroscopy confirmed improved lattice ordering through the intensified $E_2(\text{high})$ mode. FESEM and TEM analyses revealed nanoparticles of 25–37 nm with evolving spherical-to-rod-like morphology. UV–Vis spectroscopy demonstrated tunable band-gap energies (3.20–3.41 eV) and reduced Urbach energy (0.312–0.181 eV), indicating lower electronic disorder, corroborated by suppressed defect-related photoluminescence. These findings establish a direct correlation between hydrothermal temperature, defect evolution, and optical response, demonstrating a sustainable route for producing highly crystalline ZnO nanoparticles for photocatalytic, optoelectronic, ultraviolet-responsive, and sensing applications.

Keywords: Green hydrothermal synthesis; Mahua flower extract; ZnO nanoparticles; Oxygen vacancy engineering; Defect chemistry; Low-temperature crystallization

Graphical Abstract

Temperature Crystallization and Optical Tuning of ZnO

Phytochemicals

Mahua flower extract

ZnO Crystallization ♥ Oxygen

Zn^{2+}

80 °C 80-100 °C 100 °C

More vacancies Less vacancies

Optical Properties

Defect Analysis

Hamere

OL

f_t

More vacancies

f_t

O_{ads}

Fonal. T (ve next: Binding etets new)

Absorption

UV Absorbance

Band Gap

E_g

3.20-3.41 eV

Ceramic reinforcement

Zinc oxide (ZnO) is a technologically important II–VI semiconductor that has attracted considerable attention because of its wide direct band gap (~ 3.37 eV), high exciton binding energy (~ 60 meV), excellent chemical stability, environmental compatibility, and versatile optical and electronic properties. These intrinsic characteristics make ZnO an attractive functional material for diverse applications, including photocatalysis, ultraviolet photodetectors, gas sensors, transparent electronics, antimicrobial coatings, optoelectronic devices, energy storage systems, biomedical engineering, and environmental remediation. The unique combination of physicochemical stability, low toxicity, and tunable defect chemistry has further established ZnO as one of the most promising semiconductor nanomaterials for next-generation sustainable technologies [1–15].

In recent years, plant-mediated green synthesis has emerged as an environmentally benign

alternative to conventional chemical methods. Plant extracts contain abundant phytochemicals, including polyphenols, flavonoids, reducing sugars, amino acids, proteins, and organic acids, which can coordinate with metal ions and regulate nucleation, crystal growth, and surface stabilization during nanoparticle formation. Consequently, phytochemical-assisted synthesis minimizes the use of hazardous reagents while providing a sustainable route for fabricating metal oxide nanomaterials with controlled structural and optical properties [10,18,23].

Recent studies have demonstrated significant progress in the development of plant-mediated ZnO nanoparticles for photocatalytic, antibacterial, sensing, and biomedical applications. Simultaneously, defect engineering has emerged as an effective strategy for tailoring the optical and electronic properties of ZnO through controlled manipulation of oxygen vacancies, lattice disorder, and surface chemical states, which strongly influence charge-carrier separation, optical absorption, and photocatalytic activity [1–5,9,12,14,17–25]. Nevertheless, despite these advances, relatively few studies have systematically investigated how mild hydrothermal temperatures influence crystallization behavior, oxygen-vacancy evolution, lattice disorder, and optical properties using complementary structural and spectroscopic characterization techniques. Furthermore, quantitative correlations among crystal growth, defect chemistry, and optical response remain insufficiently understood, particularly under low-temperature phytochemical-assisted hydrothermal conditions.

Several plant extracts, including *Azadirachta indica*, *Aloe vera*, *Curcuma longa*, *Camellia sinensis*, *Mangifera indica*, and *Madhuca longifolia*, have been successfully employed for the green synthesis of ZnO nanoparticles. However, most previous investigations primarily focused on morphology, antibacterial activity, photocatalytic performance, or dielectric properties, whereas comparatively limited attention has been devoted to understanding the temperature-dependent evolution of crystallinity, oxygen vacancies, structural disorder, and optical characteristics under mild hydrothermal conditions. To place the present work in context, a comparison of representative plant-mediated hydrothermal synthesis routes reported in the literature with the present study is summarized in **Table 1**.

Madhuca longifolia (Mahua) flowers contain abundant phenolic compounds, flavonoids, reducing sugars, amino acids, and other oxygen-containing biomolecules that are capable of interacting with Zn^{2+} ions during hydrothermal synthesis. These phytochemicals are believed to facilitate precursor complexation, nucleation, crystal growth, and nanoparticle stabilization. Nevertheless, the individual contribution of specific phytochemical constituents during ZnO crystallization has not yet been conclusively established. Therefore, the proposed growth mechanism discussed in this work is interpreted as a literature-supported mechanism consistent with the observed structural evolution rather than as direct experimental verification.

Unlike previous studies that primarily emphasized morphology or application-oriented performance, the present investigation focuses on understanding the influence of relatively mild hydrothermal temperatures (80–100 °C) on crystal growth, defect chemistry, and optical behavior in phytochemical-assisted ZnO nanoparticles. Hydrothermal temperatures of 80–100 °C were deliberately selected to investigate whether highly crystalline ZnO nanoparticles could be synthesized under substantially milder reaction conditions than those commonly reported in the literature, thereby reducing thermal energy consumption without compromising structural quality. Particular emphasis is placed on establishing quantitative correlations among crystallite growth (XRD), morphology evolution (FESEM and TEM),

lattice disorder (Raman spectroscopy), oxygen-vacancy concentration and surface chemical states (XPS), defect-related luminescence (PL), optical band-gap energy and Urbach energy (UV–Vis spectroscopy). Such an integrated characterization provides a comprehensive understanding of temperature-dependent structural evolution that is rarely reported for phytochemical-assisted hydrothermal ZnO synthesis.

Accordingly, ZnO nanoparticles were synthesized through a Mahua-assisted hydrothermal process at **80, 90, and 100 °C** without any post-synthesis calcination treatment. The synthesized samples were systematically characterized by X-ray diffraction (XRD), field-emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), Fourier-transform infrared spectroscopy (FTIR), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), UV–visible spectroscopy, and photoluminescence (PL) spectroscopy. By integrating structural, morphological, chemical, vibrational, and optical analyses, this study establishes clear relationships among hydrothermal temperature, crystallization behavior, oxygen-vacancy evolution, structural disorder, and optical response. The findings provide new insights into low-temperature phytochemical-assisted hydrothermal crystallization of ZnO nanoparticles and contribute to the rational design of environmentally sustainable semiconductor nanomaterials for advanced photocatalytic, optoelectronic, sensing, and UV-responsive applications.

Table 1: Representative comparison of plant-mediated hydrothermal synthesis of ZnO nanoparticles reported in the literature and the present work.

Plant extract	Hydrothermal temperature (°C)	Post-calcination	Average particle size (nm)	Major characterization techniques	Primary application	Main emphasis	Limitation	Ref.
<i>Azadirachta indica</i>	150–180	Yes	30–80	XRD, SEM, FTIR, UV–Vis	Antibacterial	Structural and antibacterial properties	High synthesis temperature and post-calcination required	[18,23]
<i>Aloe vera</i>	160–180	Yes	25–70	XRD, SEM, FTIR, UV–Vis, PL	Optical and photocatalytic	Morphology and optical properties	Calcination required; limited defect characterization	[10]
<i>Curcuma longa</i>	140–180	Yes	20–60	XRD, SEM, FTIR, UV–Vis	Photocatalysis	Photocatalytic performance	Limited defect and surface chemistry analysis	[10,18]
<i>Camellia sinensis</i>	120–160	No/Yes	25–55	XRD, SEM/TEM, FTIR, UV–Vis	Antibacterial	Green synthesis and antibacterial activity	Limited correlation between XPS and optical defects	[18]
<i>Mangifera indica</i>	120–180	Yes	30–75	XRD, SEM, FTIR, UV–Vis	Structural characterization	Structural and optical properties	Temperature-dependent defect evolution has not been investigated	[18]

Plant extract	Hydrothermal temperature (°C)	Post-calcination	Average particle size (nm)	Major characterization techniques	Primary application	Main emphasis	Limitation	Ref.
<i>Madhuca longifolia</i> (recent reports)	Various	Generally, yes or higher-temperature processing	25–80	XRD, SEM, FTIR, UV–Vis	Photocatalytic and biomedical applications	Green synthesis and functional applications	Limited systematic investigation of temperature-dependent crystallization and defect evolution	[1,18,25]
Present work	80–100	No	25–37	XRD, FESEM, TEM, FTIR, Raman, XPS, UV–Vis, PL	Photocatalytic, optoelectronic, and UV-responsive materials	Systematic correlation of hydrothermal temperature with crystallization, oxygen-vacancy evolution, lattice disorder, optical band gap, photoluminescence, and Urbach energy	Control synthesis without Mahua extract was not performed	This work

Highlights

- Phytochemical-assisted hydrothermal synthesis produced phase-pure ZnO at 80–100 °C without post-calcination.
- Crystallinity increased with hydrothermal temperature, with crystallite size growing from 24.9 to 36.7 nm.
- Oxygen-vacancy concentration decreased from 26.8% to 13.5%, demonstrating effective defect modulation.
- Integrated XRD, Raman, XPS, PL, and UV–Vis analyses established temperature-dependent structure–defect–property correlations.
- Tunable optical band gap (3.29–3.43 eV) highlights the potential of ZnO for photocatalytic and optoelectronic applications.

2. Materials and Method

2.1 Materials

Zinc acetate dihydrate [$\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, $\geq 99\%$, Sigma-Aldrich] was used as the zinc precursor without further purification. Sodium hydroxide (NaOH, analytical grade, Merck) and polyethylene glycol (PEG-7000, Sigma-Aldrich) were used as received. Fresh flowers of *Madhuca longifolia* (Mahua) were collected from the local region. Deionized water was used throughout the extraction, synthesis, and purification processes [19].

2.2 Preparation of Mahua Flower Extract

Fresh Mahua flowers were thoroughly washed several times with deionized water to remove dust and other surface impurities, followed by shade drying under ambient conditions. The

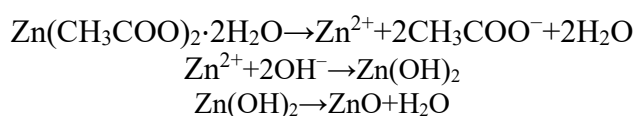
dried flowers were ground into a fine powder using a laboratory grinder. Approximately 10 g of the powdered material was dispersed in 100 mL of deionized water and heated at 80 °C for 30 min under continuous magnetic stirring to extract water-soluble phytochemical constituents.

The suspension was allowed to cool naturally to room temperature and filtered through Whatman No. 1 filter paper to obtain a clear aqueous extract. The filtrate was stored at 4 °C and used within 24 h to minimize changes in the composition of the extracted biomolecules. According to previous phytochemical studies, Mahua flowers contain phenolic compounds, flavonoids, reducing sugars, amino acids, and organic acids, which may interact with metal ions during nanoparticle formation [20]. However, the present study did not include phytochemical characterization of the extract; therefore, the discussion regarding their possible role is based on previously reported literature.

2.3 Green Hydrothermal Synthesis of ZnO Nanoparticles

ZnO nanoparticles were synthesized via a phytochemical-assisted hydrothermal method using a 25 mL Teflon-lined stainless-steel autoclave. Initially, 17.5 mL of 0.1 M aqueous zinc acetate dihydrate $[\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}]$ solution was prepared under continuous magnetic stirring until complete dissolution of the precursor. Subsequently, 5 mL of freshly prepared *Madhuca longifolia* (Mahua) flower extract was added dropwise to the precursor solution under continuous stirring to provide a phytochemical-rich reaction medium that facilitates metal-ion complexation and influences nucleation and crystal growth during hydrothermal processing [22].

To suppress particle agglomeration and improve nanoparticle dispersion, 0.16 g of polyethylene glycol (PEG-7000) was added as a non-ionic surfactant and dissolved completely under continuous stirring. Thereafter, 4 mL of 15 M NaOH solution was introduced dropwise to generate a strongly alkaline reaction medium. The final pH of the reaction mixture was maintained at approximately 12.2, promoting the precipitation of zinc hydroxide, which subsequently transformed into ZnO during hydrothermal treatment. The chemical reactions involved in the synthesis are represented as follows [23]:



The resulting homogeneous suspension was transferred into the Teflon-lined autoclave, filling approximately 90% of its total volume, and the vessel was sealed securely. Hydrothermal treatment was carried out at 80, 90, and 100 °C for 10 h in a programmable laboratory drying oven (IKA Oven 125, IKA-Werke GmbH, Germany) under autogenous pressure.

After completion of the reaction, the autoclave was allowed to cool naturally to room temperature. The precipitated ZnO nanoparticles were collected by centrifugation at 8000 rpm for 10 min and washed three times each with deionized water and absolute ethanol to remove residual precursor species and loosely adsorbed organic constituents. The purified powders were subsequently dried at 90 °C for 6 h to obtain ZnO nanopowders for further characterization.

No post-synthesis calcination treatment was applied to the obtained powders prior to structural, morphological, chemical, and optical characterization [24]. To ensure identical reaction conditions, the concentrations of the precursor, Mahua extract, PEG-7000, and NaOH were maintained constant throughout all experiments, while the hydrothermal temperature (80, 90, and 100 °C) was the only experimental variable.

Although phytochemical constituents present in Mahua flower extract are considered to facilitate metal-ion complexation, nucleation, and crystal growth, a control synthesis without Mahua extract was not performed in the present study. Therefore, the proposed role of these phytochemicals is discussed based on the observed structural evolution together with previously reported literature rather than direct experimental verification.

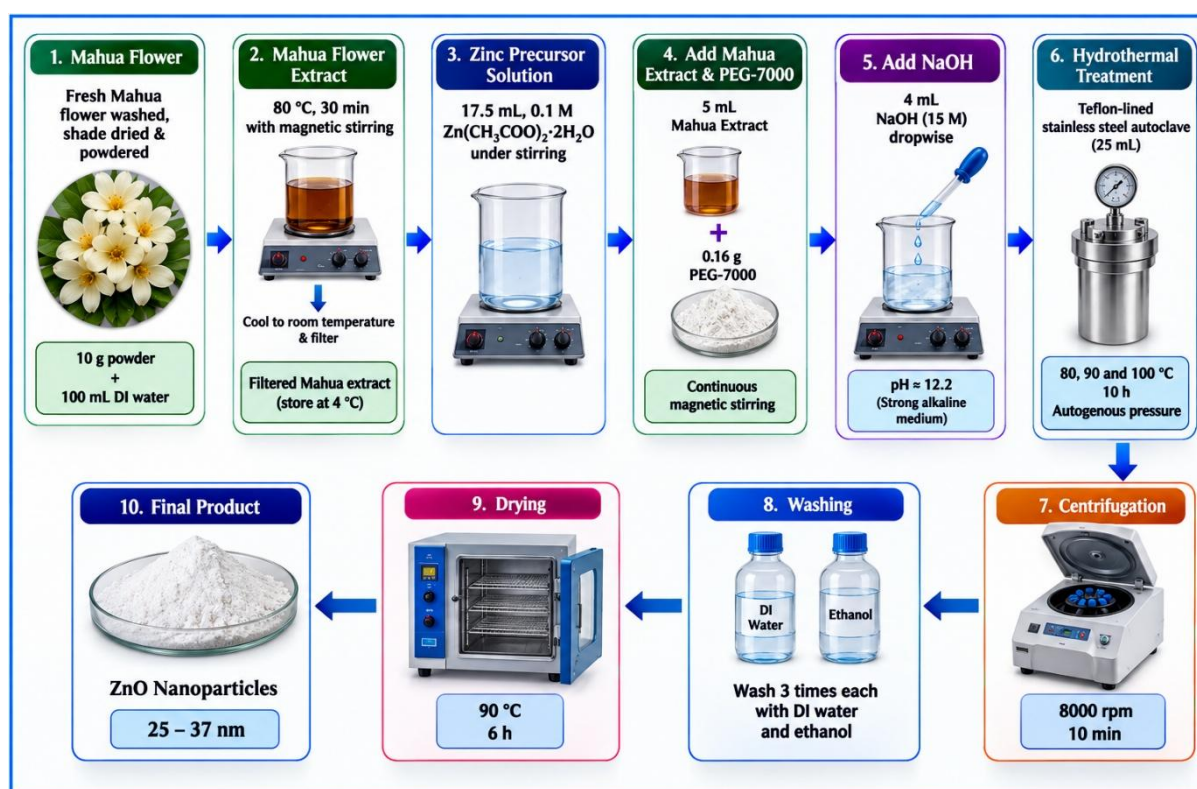


Figure 1: Schematic representation of the hydrothermal green synthesis of ZnO nanoparticles using Mahua (*Madhuca longifolia*) flower extract.

3. Results and Discussion

3.1 X-ray Diffraction Analysis

The phase purity and crystal structure of the ZnO nanoparticles synthesized at different hydrothermal temperatures were investigated by X-ray diffraction (XRD). As shown in Figure 2a, all diffraction peaks can be indexed to the hexagonal wurtzite phase of ZnO (JCPDS Card No. 79-2205), with characteristic reflections appearing at $2\theta \approx 31.7^\circ$, 34.4° , 36.2° , 47.5° , 56.6° , 62.8° , and 67.9° , corresponding to the (100), (002), (101), (102), (110), (103), and (113) crystallographic planes, respectively [23-25]. No additional diffraction peaks associated with secondary phases or impurity compounds were detected, confirming the successful formation of phase-pure ZnO nanoparticles under all hydrothermal conditions.

A progressive increase in diffraction peak intensity accompanied by a reduction in peak broadening was observed with increasing hydrothermal temperature from 80 to 100 °C (Figure 2b), indicating a continuous improvement in crystallinity. The enhanced peak sharpness suggests that elevated hydrothermal temperature promotes atomic diffusion, facilitating the growth of larger coherent diffraction domains and improving the long-range ordering of the ZnO lattice. The successful formation of highly crystalline wurtzite ZnO at temperatures as low as 80–100 °C, without any post-synthesis calcination, demonstrates the effectiveness of the phytochemical-assisted hydrothermal process.

3.1.1 Lattice Parameter Analysis

The lattice parameters of the hexagonal ZnO structure were calculated using the standard crystallographic relationship [26]:

$$\frac{1}{d^2} = \frac{4}{3} \left(\frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2}$$

where d is the interplanar spacing, (hkl) are the Miller indices, and a and c represent the lattice constants of the hexagonal unit cell.

The calculated lattice parameters were in close agreement with the standard values for hexagonal wurtzite ZnO ($a \approx 3.249$ Å and $c \approx 5.206$ Å), indicating that the crystal structure was well preserved irrespective of synthesis temperature. Only slight variations in the lattice constants were observed, suggesting minor lattice distortions arising from residual strain and defect states. Furthermore, the calculated c/a ratio remained close to the ideal value of 1.633, confirming the structural integrity of the hexagonal ZnO lattice.

3.1.2 Crystallite Size, Microstrain, and Dislocation Density

The crystallite size and lattice microstrain were determined using the Williamson–Hall (W–H) method according to the following equation [27]:

$$\beta \cos \theta = \frac{K\lambda}{D} + 4\varepsilon \sin \theta$$

The structural parameters obtained from the W–H analysis are summarized in Table 2. The average crystallite size increased systematically from 24.9 nm for the sample synthesized at 80 °C to 36.7 nm at 100 °C, corresponding to an increase of approximately 47%. This significant grain growth indicates that higher hydrothermal temperatures enhance atomic mobility, thereby promoting crystal growth and improving structural ordering. The dependence of the average crystallite size on hydrothermal synthesis temperature is presented in Figure 3. As the synthesis temperature increased from 80 to 100 °C, the crystallite size exhibited a nearly monotonic increase, confirming that elevated hydrothermal temperature promotes grain growth and improves crystallinity. The observed trend is consistent with the narrowing of the XRD diffraction peaks (Figure 2b), indicating that higher thermal energy facilitates atomic rearrangement and the formation of larger coherent diffraction domains during hydrothermal crystallization.

Simultaneously, the lattice microstrain decreased from 4.67×10^{-3} to 3.19×10^{-3} , indicating progressive relaxation of lattice distortions during hydrothermal crystallization. The reduction in residual strain suggests that elevated synthesis temperature facilitates defect annihilation and improves the structural perfection of the ZnO nanocrystals. These observations are consistent with the narrowing of the diffraction peaks and the increase in diffraction intensity observed in Figure 2.

The dislocation density (δ), calculated using [28]:

$$\delta = \frac{1}{D^2}$$

also exhibited a substantial reduction with increasing hydrothermal temperature, decreasing from 1.61×10^{-3} to $7.43 \times 10^{-4} \text{ nm}^{-2}$. The approximately 54% reduction in dislocation density confirms a significant decrease in crystallographic defects and further demonstrates the improvement in crystal quality with increasing synthesis temperature.

The simultaneous increase in crystallite size together with the reduction in lattice microstrain and dislocation density clearly indicates that hydrothermal temperature plays a crucial role in governing crystal growth and defect evolution in ZnO nanoparticles. The structural evolution observed from XRD is consistent with the reduction in oxygen-vacancy concentration obtained from XPS analysis and the enhanced lattice ordering confirmed by Raman spectroscopy, demonstrating strong correlations among crystal structure, defect chemistry, and optical properties.

Compared with previously reported plant-mediated hydrothermal syntheses, the present study achieved comparable crystallite sizes (24.9–36.7 nm) at substantially lower hydrothermal temperatures (80–100 °C) without any post-synthesis calcination treatment. These findings highlight the effectiveness of the Mahua-assisted hydrothermal route as an energy-efficient strategy for producing highly crystalline ZnO nanoparticles under mild processing conditions.

The observed improvement in structural quality is consistent with literature reports suggesting that phytochemicals present in *Madhuca longifolia* flower extract can facilitate metal-ion complexation and regulate nucleation and crystal growth during hydrothermal synthesis. Although the individual contribution of these phytochemical constituents was not experimentally isolated in the present work, the temperature-dependent structural evolution observed here supports their beneficial role in promoting the formation of phase-pure ZnO nanocrystals under mild hydrothermal conditions.

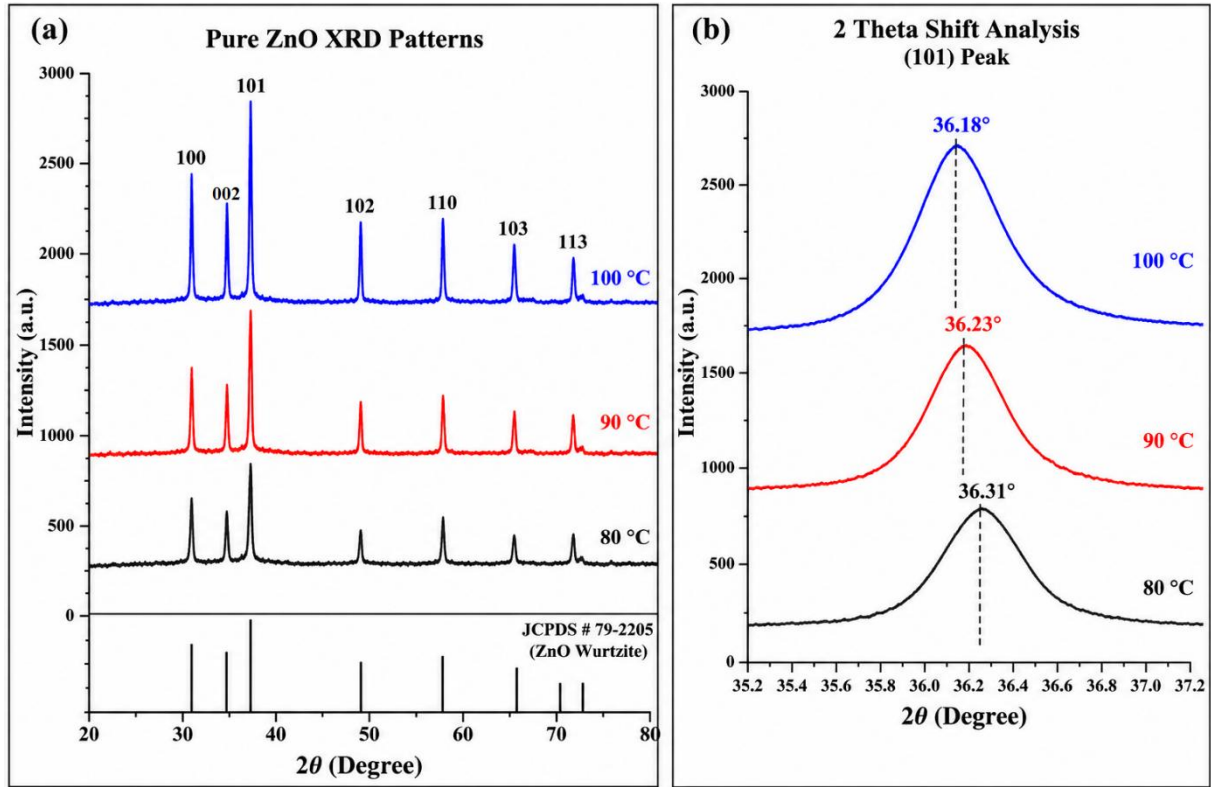


Figure 2 illustrates the XRD patterns of ZnO NPs prepared through green synthesis at three distinct temperatures: 80°C, 90°C, and 100°C. Specifically, part (a) presents the characteristic full XRD patterns for each sample, while part (b) offers a detailed comparison of the magnified (101) peak positions across the corresponding synthesis temperatures.

Table 2: Structural parameters obtained from X-ray diffraction analysis of ZnO nanoparticles synthesized at different hydrothermal temperatures, including lattice constants (a and c), c/a ratio, full width at half maximum (FWHM), Williamson–Hall crystallite size (D_{W-H}), lattice microstrain (ϵ), and dislocation density (δ), illustrating the influence of hydrothermal temperature on crystal growth, lattice relaxation, and defect evolution.

Sample	Hydrothermal Temperature (°C)	a (Å)	c (Å)	c/a	Unit Cell Volume, V (Å ³)	Internal Parameter, u	Zn–O Bond Length (Å)	FWHM (°)	Crystallite Size, D_{W-H} (nm)	Microstrain, ϵ ($\times 10^{-3}$)	Dislocation Density, δ ($\times 10^{-4}$ nm ⁻²)
Z80	80	3.257	5.210	1.599	47.90	0.382	1.976	0.35	24.92	4.67	16.10
Z90	90	3.253	5.208	1.601	47.76	0.382	1.975	0.31	28.15	4.13	12.60
Z100	100	3.249	5.206	1.602	47.62	0.382	1.974	0.24	36.67	3.19	7.43

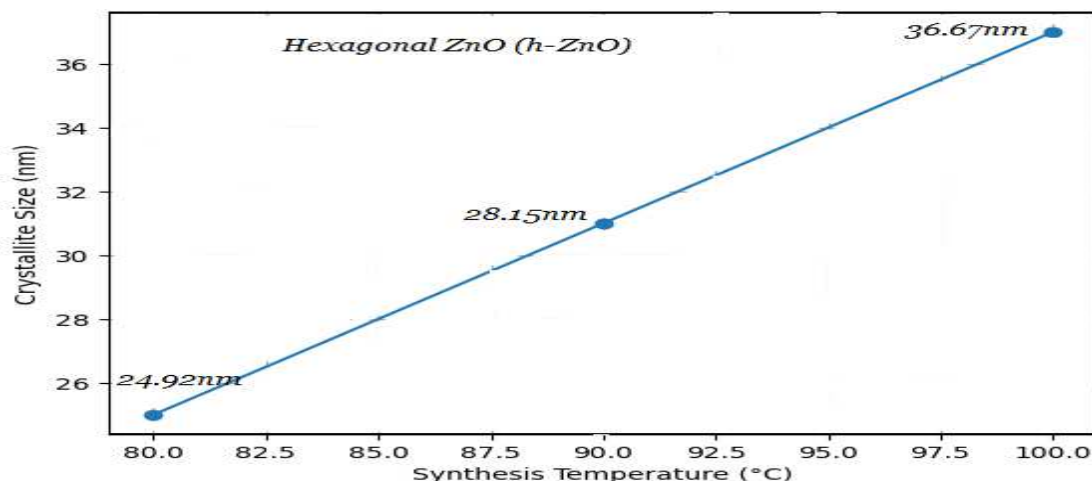


Figure 3: Variation of the average crystallite size (D101) of ZnO nanoparticles synthesized at different hydrothermal temperatures.

3.2 FESEM Morphological Investigation of ZnO Nanostructures

The morphological evolution of ZnO nanoparticles synthesized using *Madhuca longifolia* flower extract at different hydrothermal temperatures was investigated by field-emission scanning electron microscopy (FESEM) [29]. Representative FESEM micrographs together with their corresponding particle size distribution histograms are presented in Figure 4(a–f), while the quantitative morphological parameters extracted from statistical image analysis are summarized in Table 3. The FESEM observations reveal a distinct temperature-dependent evolution in particle morphology, whereas the statistical analysis confirms a systematic increase in particle size with increasing hydrothermal temperature.

The ZnO nanoparticles synthesized at 80 °C (Z80) (Figure 4a) predominantly consist of densely agglomerated quasi-spherical nanoparticles with rough surface morphology and indistinct particle boundaries. Such aggregation is attributed to rapid nucleation accompanied by limited atomic diffusion under relatively low hydrothermal temperature. Statistical analysis of 128 randomly selected nanoparticles yielded an average particle size of 24.8 ± 3.2 nm, with a particle size range of 18–32 nm, as summarized in Table 3. The corresponding histogram (Figure 4b) follows a log-normal distribution, indicating diffusion-controlled particle growth. The relatively small particle size is in close agreement with the lower crystallite size determined from the Williamson–Hall analysis, suggesting limited crystal growth under these synthesis conditions.

Upon increasing the hydrothermal temperature to 90 °C (Z90), a significant morphological refinement is observed (Figure 4c). The nanoparticles transform into well-developed polygonal and plate-like structures with smoother surfaces, clearly distinguishable crystal facets, and improved particle separation. The corresponding particle size histogram (Figure 4d) remains well fitted by a log-normal distribution. Quantitative analysis (Table 3) indicates an average particle size of 28.5 ± 3.8 nm, with particle diameters ranging from 21 to 38 nm. The increase in particle size and improved morphological uniformity reflect enhanced crystal growth due to increased atomic mobility during hydrothermal synthesis. These observations correlate well with the increase in crystallite size and reduction in lattice strain obtained from XRD analysis.

Further increasing the hydrothermal temperature to 100 °C (Z100) results in the formation of predominantly elongated rod-like and prismatic ZnO nanostructures (Figure 4e). The nanorods exhibit smooth surfaces, well-defined crystal boundaries, and relatively uniform dimensions, reflecting anisotropic crystal growth under optimized hydrothermal conditions. The particle size histogram (Figure 4f) shows a slightly broader but symmetric log-normal distribution. As listed in Table 2, the average particle size increases to 35.4 ± 4.1 nm, with particle sizes distributed between 27 and 46 nm. This increase in particle size is attributed to enhanced dissolution–recrystallization kinetics and preferential crystal growth at higher hydrothermal temperatures.

The quantitative morphological parameters summarized in Table 3 clearly demonstrate a gradual increase in average particle size from 24.8 ± 3.2 nm (Z80) to 28.5 ± 3.8 nm (Z90) and 35.4 ± 4.1 nm (Z100). Simultaneously, the particle morphology evolves from agglomerated quasi-spherical nanoparticles to well-defined polygonal structures and finally to anisotropic rod-like nanostructures. The particle size distributions for all samples exhibit log-normal characteristics, indicating that the particle growth process is primarily governed by diffusion-controlled nucleation and growth mechanisms.

The observed morphological evolution can be explained by the hydrothermal crystal growth mechanism [30]. At lower synthesis temperatures, rapid nucleation generates numerous small nanoparticles that readily agglomerate because of their high surface energy. Increasing the hydrothermal temperature enhances ionic diffusion, facilitating dissolution–reprecipitation and oriented crystal growth, thereby producing larger and more uniform ZnO nanostructures. In addition, phytochemicals present in *Madhuca longifolia* flower extract act as natural capping and stabilizing agents, regulating nucleation, suppressing excessive aggregation, and promoting controlled anisotropic growth.

Importantly, the average particle sizes determined from FESEM analysis (Table 3) exhibit excellent agreement with the crystallite sizes obtained from Williamson–Hall analysis (24.9–36.7 nm), indicating that the synthesized ZnO particles consist predominantly of highly crystalline domains with limited interparticle aggregation. The close correspondence between structural and morphological analyses confirms that hydrothermal temperature effectively controls both crystal growth and particle morphology in the green synthesis of ZnO nanoparticles.

The FESEM investigation demonstrates that hydrothermal temperature is the primary parameter governing the nucleation, growth, and morphological evolution of biosynthesized ZnO nanoparticles [30]. The transformation from agglomerated quasi-spherical particles to faceted polygonal structures and finally to anisotropic rod-like nanostructures, together with the quantitative particle size analysis presented in **Table 3**, confirms the progressive enhancement of crystal growth with increasing synthesis temperature. Such controlled morphological evolution is expected to be advantageous for optical and optoelectronic applications owing to the improved particle uniformity and reduced structural disorder.

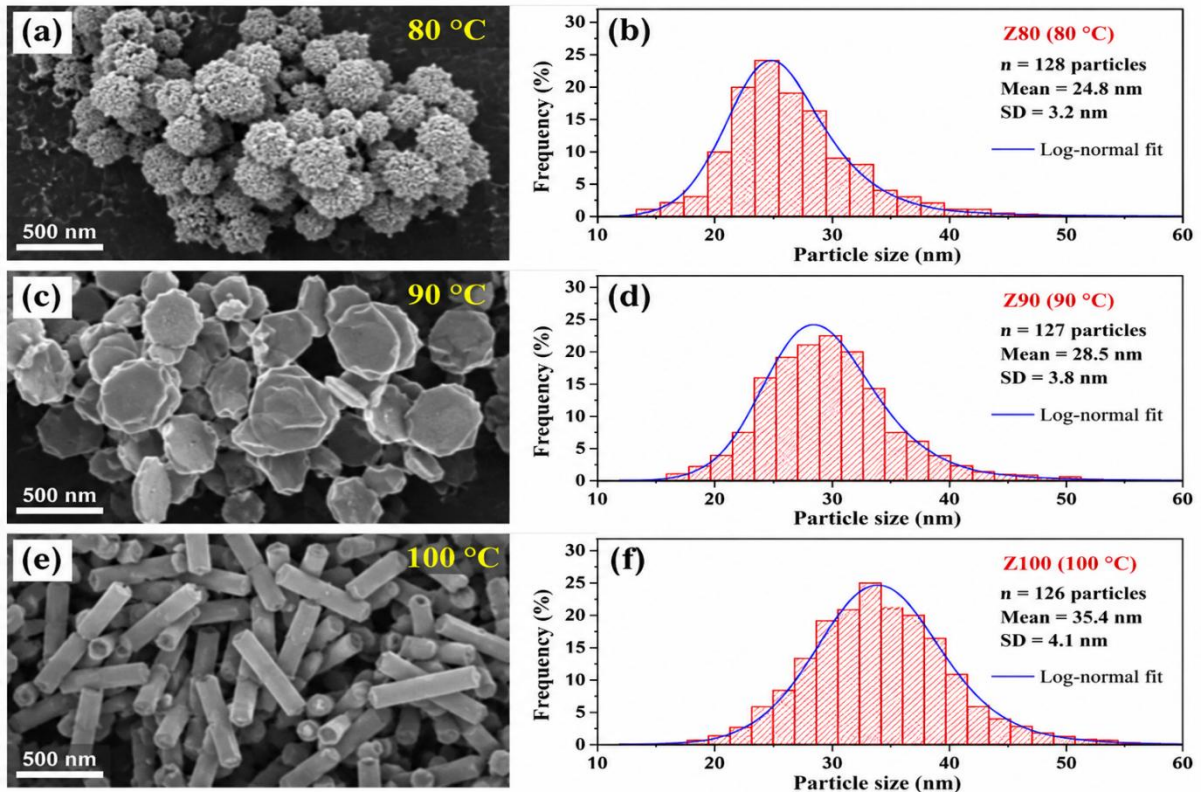


Figure 4 displays the High-resolution electron micrographs of ZnO samples. These images provide insights into the morphology of the nanoparticles synthesized at various temperatures: (a) 80 °C, (b) 90 °C, and (c) 100 °C.

Table 3: Morphological parameters of biosynthesized ZnO nanoparticles obtained from FESEM image analysis.

Sample	Hydrothermal Temperature (°C)	Average Particle Size (nm)	Particle Size Range (nm)	Standard Deviation (nm)	Number of Particles Analyzed (n)	Dominant Morphology
Z80	80	24.8 ± 3.2	18–32	3.2	128	Agglomerated quasi-spherical
Z90	90	28.5 ± 3.8	21–38	3.8	127	Polygonal / plate-like
Z100	100	35.4 ± 4.1	27–46	4.1	126	Rod-like / prismatic

3.2.1 Quantitative Particle Size Distribution and Growth Mechanism

To quantitatively evaluate the influence of hydrothermal temperature on particle growth, statistical image analysis was performed using the FESEM micrographs shown in Figure 4. More than 120 randomly selected nanoparticles were analyzed for each sample (Z80, Z90, and Z100) to ensure statistical reliability and minimize sampling bias. The corresponding particle size distribution histograms (Figure 4b, d, and f) exhibit narrow unimodal distributions that are well described by a log-normal distribution function, which is characteristic of nanoparticles formed through nucleation- and diffusion-controlled crystal growth mechanisms. The log-normal probability density function is expressed as [31]:

$$f(D) = \frac{1}{D\sigma\sqrt{2\pi}} \exp\left[-\frac{(\ln D - \ln D_0)^2}{2\sigma^2}\right]$$

where D is the particle diameter, D_0 is the median particle size, and σ is the standard deviation of the logarithmic particle size distribution.

The quantitative morphological parameters obtained from the fitted distributions are summarized in Table 2. The average particle size increased systematically with hydrothermal temperature, from 24.8 ± 3.2 nm for Z80 to 28.5 ± 3.8 nm for Z90 and 35.4 ± 4.1 nm for Z100. Similarly, the particle size range broadened from 18–32 nm (Z80) to 27–46 nm (Z100), indicating progressive crystal growth under elevated hydrothermal conditions. The gradual shift of the histogram maxima toward larger particle sizes further confirms that increasing synthesis temperature promotes the growth of ZnO nanoparticles while maintaining a relatively narrow particle size distribution.

To further assess the particle size uniformity, the polydispersity index (PDI) was calculated using [32]:

$$PDI = \left(\frac{\sigma_D}{\bar{D}}\right)^2$$

where σ_D is the standard deviation of the particle diameter in the linear scale and $\bar{D}$ is the average particle size. The calculated PDI values are 0.017 for Z80, 0.018 for Z90, and 0.013 for Z100 (Table 2), indicating narrow particle size distributions for all samples. The slightly lower PDI obtained for Z100 suggests improved particle size uniformity at higher hydrothermal temperatures, reflecting enhanced control over nucleation and crystal growth during the biosynthesis process.

The observed log-normal particle size distributions indicate that ZnO nanoparticle growth is primarily governed by diffusion-controlled crystal growth, in which initially formed nuclei progressively grow through the incorporation of dissolved Zn^{2+} and OH^- species [33]. As the hydrothermal temperature increases, enhanced ionic mobility accelerates Ostwald ripening, whereby smaller crystallites dissolve and redeposit onto larger particles, leading to an increase in average particle size. Simultaneously, thermally assisted coalescence and dissolution–reprecipitation processes promote anisotropic crystal growth, resulting in the formation of well-defined rod-like nanostructures at 100 °C.

The phytochemicals present in *Madhuca longifolia* flower extract are also expected to play a significant role in regulating crystal growth. Hydroxyl- and carbonyl-containing biomolecules can selectively adsorb onto specific ZnO crystal facets, acting as natural capping and stabilizing agents that suppress excessive particle aggregation while promoting controlled nucleation and directional crystal growth. Consequently, nanoparticles synthesized at higher temperatures exhibit improved morphological uniformity and well-developed crystal architectures.

Furthermore, the average particle sizes determined from FESEM image analysis (24.8–35.4 nm) show excellent agreement with the crystallite sizes obtained from Williamson–Hall analysis (24.9–36.7 nm). This close correspondence suggests that the synthesized ZnO

particles consist predominantly of highly crystalline domains, with only limited aggregation of multiple crystallites. The strong agreement between the structural and morphological analyses confirms that hydrothermal temperature effectively governs crystal growth, particle morphology, and structural ordering in the green synthesis of ZnO nanoparticles.

3.3 Transmission Electron Microscopy (TEM) Investigation of ZnO Nanostructures

The internal microstructure and particle morphology of the biosynthesized ZnO nanoparticles were further examined by transmission electron microscopy (TEM). Representative TEM micrographs together with their corresponding particle size distribution histograms are presented in Figure 5(a–f), while the quantitative particle size statistics obtained from TEM image analysis are summarized in Table 4. The TEM analysis provides direct evidence of the temperature-dependent evolution of particle morphology and confirms the trend observed from FESEM and XRD analyses [34,35].

The Z80 sample synthesized at 80 °C (Figure 5a) consists predominantly of nearly spherical nanoparticles with moderate agglomeration caused by the high surface energy of the nanosized particles. The corresponding particle size distribution histogram (Figure 5d) exhibits a narrow log-normal distribution centered at 24.92 ± 5.34 nm. As summarized in Table 3, most nanoparticles are distributed within the 20–30 nm size range, indicating that crystal growth remains limited at the lower hydrothermal temperature. The measured particle size is in excellent agreement with the FESEM-derived average particle size (24.8 ± 3.2 nm) and the Williamson–Hall crystallite size (24.9 nm), confirming the consistency of the structural and morphological analyses.

When the hydrothermal temperature is increased to 90 °C, a distinct morphological refinement is observed (Figure 5b). The nanoparticles become more uniform with well-developed polygonal and faceted morphologies, accompanied by a noticeable reduction in particle agglomeration. The corresponding histogram (Figure 5e) yields an average particle size of 28.15 ± 9.59 nm. The quantitative distribution presented in Table 3 reveals that the majority of particles are concentrated within the 25–35 nm interval, demonstrating progressive crystal growth and improved particle uniformity. This increase in particle size agrees closely with the FESEM measurements (28.5 ± 3.8 nm) and the increase in crystallite size obtained from XRD analysis.

Further increasing the hydrothermal temperature to 100 °C results in the formation of larger and well-defined ZnO nanostructures with improved particle boundaries and reduced structural irregularities (Figure 5c). The particle size distribution histogram (Figure 5f) is shifted toward larger diameters, yielding an average particle size of 36.67 ± 9.59 nm. As listed in Table 4, most particles are distributed within the 30–45 nm range, indicating enhanced crystal growth at elevated temperature. The increase in particle size is consistent with the FESEM observations (35.4 ± 4.1 nm) and the Williamson–Hall crystallite size (36.7 nm), confirming that hydrothermal temperature effectively promotes crystal growth without significant secondary particle aggregation.

The quantitative particle size distribution presented in Table 4 clearly demonstrates a systematic increase in the average particle size from 24.92 nm (Z80) to 28.15 nm (Z90) and 36.67 nm (Z100) with increasing hydrothermal temperature. Simultaneously, the particle size distribution shifts toward larger size intervals, indicating enhanced crystal growth kinetics under hydrothermal conditions. The relatively narrow distributions observed for all three

samples suggest controlled nucleation and particle growth, which can be attributed to the stabilizing action of phytochemicals present in the *Madhuca longifolia* flower extract.

The observed temperature-dependent particle growth can be explained by the hydrothermal crystallization mechanism [36]. At lower temperatures, rapid nucleation produces numerous small nanoparticles with limited crystal growth. Increasing the hydrothermal temperature enhances ionic diffusion and dissolution–reprecipitation processes, promoting Ostwald ripening and directional crystal growth. In addition, hydroxyl- and carbonyl-containing phytochemicals present in the Mahua flower extract selectively adsorb on the ZnO surface, acting as natural capping agents that regulate nucleation and suppress excessive particle aggregation. Consequently, larger, more uniform, and structurally ordered nanoparticles are obtained at higher synthesis temperatures.

The TEM observations, together with the quantitative particle size analysis summarized in Table 4, are in excellent agreement with the FESEM and XRD results. The close correspondence between the TEM particle sizes (24.92–36.67 nm), FESEM particle sizes (24.8–35.4 nm), and Williamson–Hall crystallite sizes (24.9–36.7 nm) demonstrates the reliability of the synthesis process and confirms that increasing hydrothermal temperature promotes the formation of highly crystalline and morphologically uniform ZnO nanoparticles.

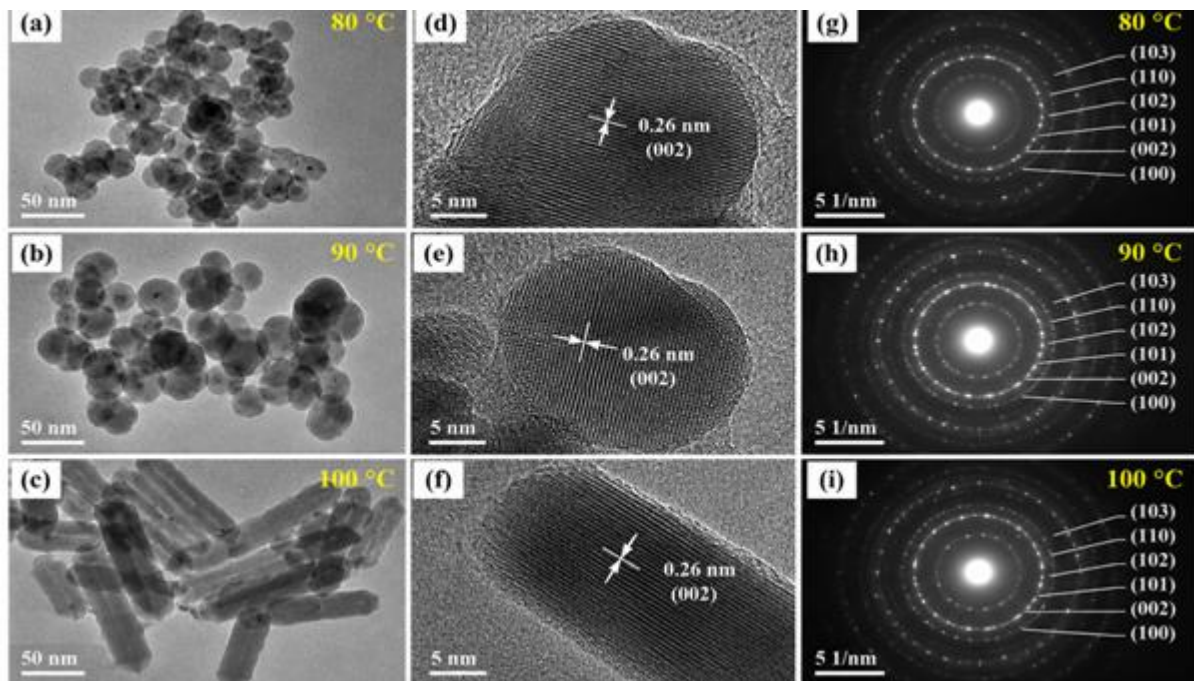


Figure 5: Transmission electron microscopy characterization of ZnO nanoparticles synthesized using *Madhuca longifolia* flower extract at different hydrothermal temperatures: (a–c) TEM images of Z80, Z90, and Z100 samples, respectively; (d–f) corresponding HRTEM images showing lattice fringes; and (g–i) SAED patterns confirming the hexagonal wurtzite crystal structure.

Table 4: Quantitative particle size distribution of biosynthesized ZnO nanoparticles obtained from TEM analysis, showing particle size intervals, corresponding class midpoints, particle counts, and relative frequency.

Particle Size Range (nm)	Midpoint (nm)	Z80 (24.92 ± 5.34 nm) Count	Relative Frequency (%)	Z90 (28.15 ± 9.59 nm) Count	Relative Frequency (%)	Z100 (36.67 ± 9.59 nm) Count	Relative Frequency (%)
10–15	12.5	2	1.7	1	0.8	0	0.0
15–20	17.5	15	12.5	6	5.0	2	1.7
20–25	22.5	39	32.5	18	15.0	7	5.8
25–30	27.5	42	35.0	36	30.0	15	12.5
30–35	32.5	18	15.0	29	24.2	24	20.0
35–40	37.5	4	3.3	18	15.0	29	24.2
40–45	42.5	0	0.0	8	6.7	23	19.2
45–50	47.5	0	0.0	3	2.5	12	10.0
50–55	52.5	0	0.0	1	0.8	5	4.2
55–60	57.5	0	0.0	0	0.0	2	1.7
Total	—	120	100	120	100	120	100

3.4 Fourier Transform Infrared (FTIR) Spectroscopic Analysis

The FTIR spectra of the *Madhuca longifolia* (Mahua) flower extract and the biosynthesized ZnO nanoparticles synthesized at hydrothermal temperatures of 80, 90, and 100 °C are presented in **Figure 6**. The spectra provide valuable information regarding the phytochemical constituents involved in nanoparticle formation and the structural evolution of ZnO with increasing hydrothermal temperature. In particular, the progressive changes in the organic functional groups and Zn–O vibrational modes provide direct evidence for the conversion of Zn²⁺ precursor species into crystalline ZnO and elucidate the role of plant-derived biomolecules during the green synthesis process.

The FTIR spectrum of the Mahua flower extract (**Figure 6a**) exhibits a broad absorption band in the 3000–3500 cm^{−1} region, corresponding to the stretching vibration of hydrogen-bonded hydroxyl (O–H) groups originating from phenols, alcohols, carbohydrates, and other polyhydroxylated phytochemicals. Additional absorption bands centered near 1652 cm^{−1} and 1598 cm^{−1} are attributed to carbonyl (C=O), amide, and aromatic C=C vibrations associated with flavonoids, phenolic acids, proteins, and tannins. The bands observed in the 1281–1035 cm^{−1} region arise from C–O, C–O–C, and C–N stretching vibrations of alcohols, ethers, polysaccharides, and amino-containing biomolecules [37]. These oxygen-rich functional groups possess strong coordination ability toward Zn²⁺ ions and therefore serve as natural chelating agents during the initial stage of hydrothermal synthesis. Their adsorption on the growing ZnO nuclei also limits uncontrolled aggregation, enabling controlled nucleation and particle growth.

After hydrothermal treatment, the FTIR spectra of the ZnO nanoparticles (**Figure 6b–d**) exhibit significant modifications compared with the pristine plant extract, confirming the participation of these phytochemicals in nanoparticle formation. For the Z80 sample, the persistence of the broad O–H stretching band at 3443 cm^{−1} together with absorption bands near 1620 cm^{−1} and 1125–991 cm^{−1} indicates that a fraction of the phytochemical molecules remains adsorbed on the nanoparticle surface. These residual biomolecules function as surface-stabilizing ligands that prevent excessive particle coalescence during the early stages of crystal growth. Simultaneously, the emergence of a distinct absorption band near 620

cm^{-1} , assigned to the Zn–O stretching vibration, confirms the successful formation of the ZnO framework.

As the hydrothermal temperature increases to **90 °C**, the intensity of the hydroxyl-, carbonyl-, and C–O-related absorption bands decreases noticeably, whereas the Zn–O vibration remains clearly identifiable. This evolution indicates that increasing thermal energy accelerates the hydrolysis and dehydration of $\text{Zn}(\text{OH})_2$ intermediates, promoting the conversion of Zn–organic complexes into ZnO. The partial removal of surface-bound phytochemicals exposes additional crystal facets, facilitating atomic diffusion and directional crystal growth [38]. These spectroscopic observations are fully consistent with the FESEM and TEM results, which reveal the transformation from agglomerated quasi-spherical particles to well-developed faceted nanoparticles, as well as with the XRD results showing increased crystallite size and reduced lattice strain.

The spectrum of the **Z100** sample exhibits the weakest organic absorption bands, demonstrating that most of the phytochemical residues have been removed during hydrothermal crystallization. In contrast, the Zn–O stretching vibrations in the **423–479 cm^{-1}** region become more pronounced, indicating the progressive development of the Zn–O network. Although FTIR alone cannot be used to quantify crystallinity, the strengthening of the Zn–O vibration together with the substantial reduction of organic functional groups suggests the formation of a more ordered Zn–O framework. This interpretation agrees well with the sharper XRD diffraction peaks, the improved crystal morphology observed by FESEM and TEM, and the enhanced lattice ordering evidenced by Raman spectroscopy.

The temperature-dependent FTIR evolution also provides important insight into the green synthesis mechanism. Initially, hydroxyl, carbonyl, and ether groups present in the Mahua flower extract coordinate with Zn^{2+} ions, forming Zn–organic complexes that regulate nucleation and suppress uncontrolled particle growth. During hydrothermal treatment, these complexes undergo hydrolysis to $\text{Zn}(\text{OH})_2$, followed by dehydration to produce crystalline ZnO. Increasing hydrothermal temperature accelerates this transformation, simultaneously removing residual organic species and promoting the formation of a continuous Zn–O lattice. Consequently, higher temperatures favour anisotropic crystal growth, leading to the larger particle sizes and rod-like morphologies observed in the FESEM and TEM analyses.

The FTIR results are strongly supported by the complementary characterization techniques employed in this work. The gradual reduction of organic functional groups correlates directly with the increase in crystallite size determined by XRD, the evolution of particle morphology observed by FESEM and TEM, the enhancement of lattice ordering revealed by Raman spectroscopy, and the reduction in oxygen-related defect species identified by XPS. Collectively, these results demonstrate that the phytochemicals present in *Madhuca longifolia* flower extract perform a dual function as both complexing agents for Zn^{2+} ions and surface stabilizers during nanoparticle growth, while increasing hydrothermal temperature promotes the removal of organic residues, improves structural ordering, and facilitates the formation of highly crystalline ZnO nanoparticles.

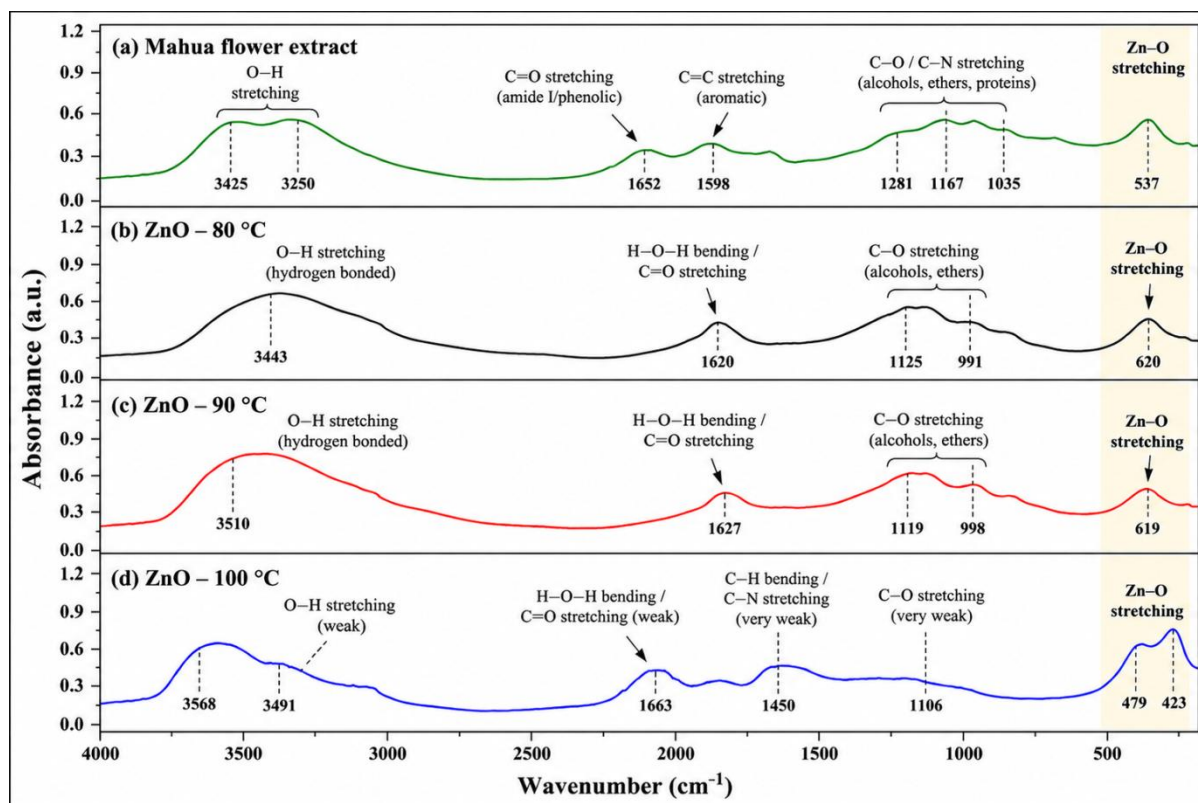


Figure 6: FTIR spectra of (a) *Madhuca longifolia* flower extract and ZnO nanoparticles synthesized hydrothermally at (b) 80 °C (Z80), (c) 90 °C (Z90), and (d) 100 °C (Z100).

3.5 Raman Spectroscopic Analysis

Raman spectroscopy was employed to investigate the lattice vibrational characteristics, crystal quality, and defect evolution of the biosynthesized ZnO nanoparticles synthesized at different hydrothermal temperatures [39]. The Raman spectra recorded in the range of **100–1500 cm^{-1}** are presented in **Figure 7**. All samples exhibit the characteristic first-order Raman modes of the hexagonal wurtzite ZnO structure, confirming the phase purity and crystal structure previously established by X-ray diffraction analysis.

The dominant Raman band located at approximately **437 cm^{-1}** is assigned to the non-polar **$E_2(\text{high})$** phonon mode, which originates from the vibration of oxygen atoms in the hexagonal wurtzite ZnO lattice. This vibration is widely recognized as the fingerprint of highly crystalline ZnO. The **$E_2(\text{high})$** peak remains nearly unchanged at approximately **437 cm^{-1}** for all samples, indicating negligible residual lattice stress and confirming that variation in hydrothermal temperature does not induce measurable lattice distortion. However, the progressive increase in the intensity and sharpening of the **$E_2(\text{high})$** mode with increasing synthesis temperature indicates enhanced crystallinity, improved long-range lattice ordering, and reduced phonon scattering arising from structural imperfections. These observations agree well with the XRD results, which demonstrate an increase in crystallite size together with a reduction in microstrain and dislocation density as the hydrothermal temperature increases.

A weak Raman band observed near **330 cm^{-1}** corresponds to the second-order **$E_2(\text{high})$ – $E_2(\text{low})$** multiphonon scattering process, further confirming the formation of the well-crystallized wurtzite ZnO phase. The persistence of this second-order phonon mode in all

samples indicates that the hydrothermal synthesis successfully produces crystalline ZnO without detectable secondary phases.

The broad Raman band appearing in the **580–585 cm⁻¹** region is assigned to the defect-sensitive **A₁(LO)/E₁(LO)** longitudinal optical phonon modes. These modes are primarily associated with intrinsic lattice defects, including oxygen vacancies (V_o), zinc interstitials (Zn_i), and local lattice disorder. A systematic reduction in the intensity of the LO mode is observed with increasing hydrothermal temperature, indicating progressive suppression of defect-related phonon scattering and improvement in crystal quality. The weaker LO vibration observed for the Z100 sample suggests that elevated hydrothermal temperatures effectively reduce the concentration of intrinsic lattice defects through enhanced crystal growth and defect healing.

The temperature-dependent evolution of the Raman spectra provides valuable insight into the hydrothermal crystallization mechanism of the Mahua-mediated ZnO nanoparticles. At relatively low hydrothermal temperatures, rapid nucleation produces numerous small crystallites containing a high density of structural imperfections and oxygen-deficient regions [40]. Increasing the hydrothermal temperature enhances ionic diffusion, dissolution–reprecipitation processes, and dehydration of Zn(OH)₂ intermediates, allowing Zn and O atoms to occupy thermodynamically favorable lattice positions. Consequently, stronger Zn–O bonding is established, oxygen-deficient sites are progressively eliminated, and a highly ordered wurtzite crystal lattice is formed. This structural evolution is reflected by the enhanced **E₂(high)** phonon mode and the simultaneous suppression of the defect-related LO vibration.

The Raman results exhibit excellent agreement with the complementary characterization techniques employed in this work [41]. The enhancement of the **E₂(high)** mode is consistent with the improved crystallinity, increased crystallite size, and reduced lattice strain obtained from XRD, as well as the well-defined particle morphology observed by FESEM and HRTEM analyses. Furthermore, the reduction of the **A₁(LO)/E₁(LO)** defect mode closely correlates with the O 1s XPS analysis, which reveals a systematic decrease in oxygen-vacancy concentration from **26.8% (Z80)** to **13.5% (Z100)**. The progressive removal of hydroxyl- and carbonyl-containing phytochemical residues observed in the FTIR spectra further supports the formation of a stronger Zn–O framework during hydrothermal crystallization. Likewise, the suppression of the defect-related Raman mode agrees well with the reduced visible photoluminescence intensity, confirming fewer oxygen-vacancy-assisted radiative recombination centers, while the simultaneous decrease in Urbach energy obtained from UV–Vis spectroscopy indicates reduced electronic disorder and fewer localized defect states near the band edges.

Overall, the Raman investigation demonstrates that increasing hydrothermal temperature significantly enhances lattice ordering, strengthens Zn–O bonding, and suppresses intrinsic lattice defects in Mahua-mediated ZnO nanoparticles. The excellent agreement between Raman, XRD, FTIR, FESEM, HRTEM, XPS, UV–Vis, and photoluminescence analyses provides compelling evidence that hydrothermal temperature plays a decisive role in controlling the crystallinity, defect chemistry, and optical quality of the biosynthesized ZnO nanostructures.

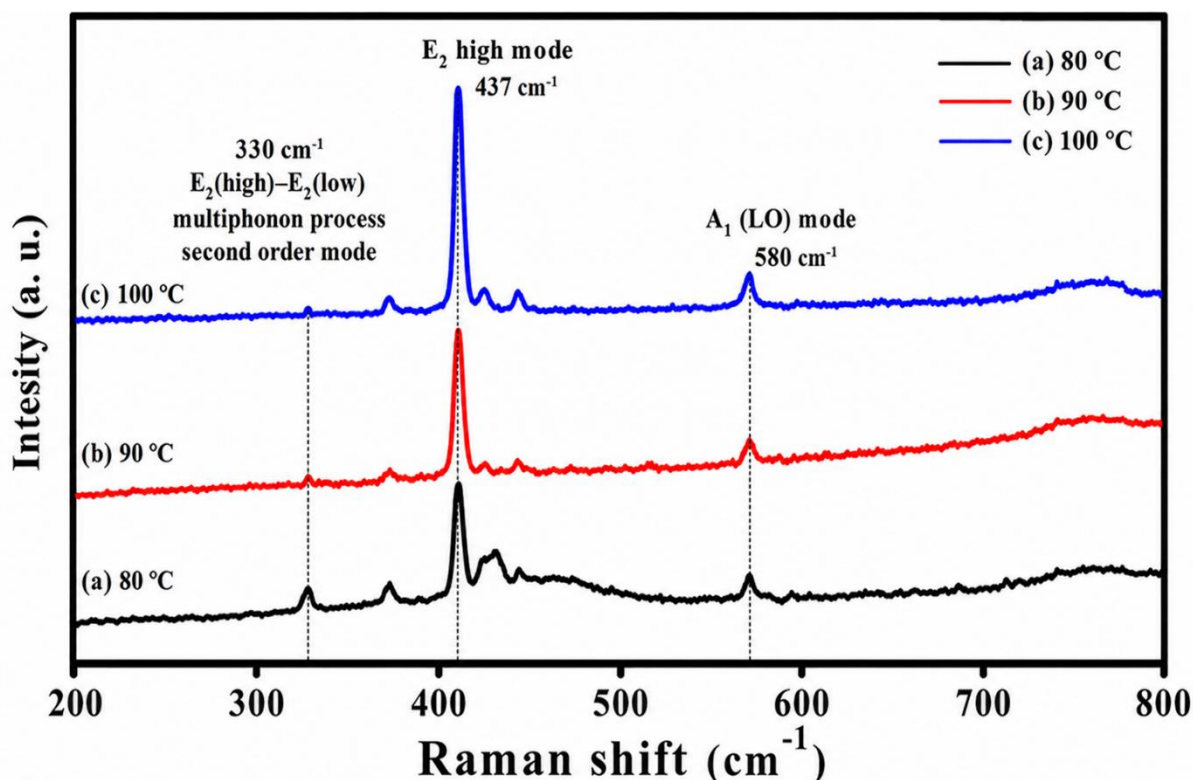


Figure 7: Raman spectra of biosynthesized ZnO nanoparticles synthesized using *Madhuca longifolia* flower extract at hydrothermal temperatures of 80 °C (Z80), 90 °C (Z90), and 100 °C (Z100).

3.6 X-ray Photoelectron Spectroscopy (XPS) Analysis

X-ray photoelectron spectroscopy (XPS) was employed to investigate the surface chemical composition, oxidation states, and defect chemistry of the biosynthesized ZnO nanoparticles prepared at different hydrothermal temperatures [41,42]. The high-resolution **Zn 2p** and **O 1s** spectra are presented in **Figure 8**. XPS provides direct evidence for the chemical evolution of the ZnO lattice and enables quantitative evaluation of oxygen-vacancy-related defects, which play a critical role in determining the structural and optical properties of ZnO nanostructures.

3.6.1 Zn 2p Core-Level Analysis

The high-resolution Zn 2p spectra of the ZnO nanoparticles synthesized at 80, 90, and 100 °C are shown in Figure 8(a). All samples exhibit two well-defined photoelectron peaks centered at approximately 1021.6 eV and 1044.7 eV, corresponding to the Zn 2p_{3/2} and Zn 2p_{1/2} core levels, respectively. The measured spin–orbit splitting energy of approximately 23.1 eV agrees well with the standard value reported for hexagonal wurtzite ZnO, confirming that zinc exists exclusively in the Zn²⁺ oxidation state [43]. The detailed binding energies and spin–orbit splitting values for all samples are summarized in Table 5. The absence of additional peaks associated with metallic Zn or secondary zinc oxide phases further demonstrates the high phase purity of the biosynthesized nanoparticles.

A slight shift of both Zn 2p peaks toward higher binding energy with increasing hydrothermal temperature is observed, accompanied by a gradual narrowing of the spectral profile [44]. This behavior suggests a progressive strengthening of the Zn–O chemical bonds and improved chemical homogeneity within the ZnO lattice. The enhanced Zn–O interaction originates from more complete hydrolysis of Zn²⁺ precursor complexes and improved

crystallization under elevated hydrothermal conditions, which facilitate the formation of a well-ordered Zn–O framework.

These observations correlate closely with the FTIR results, where the gradual disappearance of hydroxyl- and carbonyl-containing phytochemical residues together with the strengthening of the Zn–O stretching vibration indicates progressive removal of organic ligands and completion of Zn–O bond formation. Similarly, the increase in crystallite size and reduction in lattice strain obtained from XRD, together with the improved particle morphology observed by FESEM and TEM, demonstrate that increasing hydrothermal temperature promotes structural ordering throughout the ZnO nanoparticles. Furthermore, the enhanced lattice quality is consistent with the increased intensity of the Raman $E_2(\text{high})$ phonon mode, confirming improved crystallinity.

Overall, the Zn 2p analysis demonstrates that increasing hydrothermal temperature significantly improves lattice stabilization and chemical ordering without altering the oxidation state of zinc, resulting in highly crystalline ZnO nanoparticles with superior structural integrity.

Table 5: Binding energies and spin–orbit splitting parameters obtained from Zn 2p XPS spectra of biosynthesized ZnO nanoparticles synthesized at different hydrothermal temperatures.

Sample	Zn 2p _{3/2} Binding Energy (eV)	Zn 2p _{1/2} Binding Energy (eV)	Spin–Orbit Splitting (eV)	Oxidation State	Observation
Z80 (80 °C)	1021.6	1044.7	23.1	Zn ²⁺	Stoichiometric ZnO with slight lattice disorder
Z90 (90 °C)	1021.6	1044.7	23.1	Zn ²⁺	Improved chemical homogeneity and Zn–O bonding
Z100 (100 °C)	1021.6	1044.7	23.1	Zn ²⁺	Highly crystalline ZnO with enhanced lattice ordering

3.6.2 O 1s Core-Level Analysis and Defect Evolution

The deconvoluted O 1s spectra of the ZnO nanoparticles synthesized at different hydrothermal temperatures are presented in **Figure 8(b)**. The asymmetric O 1s envelope was successfully resolved into three chemically distinct components corresponding to lattice oxygen (O_L), oxygen-vacancy-related oxygen (O_V), and surface-adsorbed oxygen species (O_{ads}).

The low-binding-energy component located at 529.6–529.8 eV is assigned to lattice oxygen (O_L) associated with Zn–O bonds in the hexagonal wurtzite structure. This component represents oxygen atoms occupying regular lattice sites and therefore reflects the degree of structural ordering within the ZnO crystal. The progressive increase in the lattice oxygen contribution with increasing hydrothermal temperature indicates the formation of a more stoichiometric and structurally ordered ZnO framework.

The intermediate component centered at approximately 531.3–531.5 eV corresponds to oxygen-vacancy-related defect states (O_V). These defects originate from oxygen-deficient lattice sites and are responsible for localized electronic states, lattice disorder, and defect-

assisted optical transitions. Quantitative peak-area analysis (Table 4) reveals that the oxygen-vacancy concentration decreases systematically from 26.8% for Z80 to 19.4% for Z90 and 13.5% for Z100. The reduction in oxygen vacancies can be attributed to enhanced ionic diffusion and more complete crystallization during hydrothermal synthesis. At elevated temperatures, Zn and O atoms acquire sufficient mobility to occupy thermodynamically stable lattice positions, thereby minimizing oxygen-deficient regions and suppressing the formation of intrinsic lattice defects. Simultaneously, improved dehydration of $\text{Zn}(\text{OH})_2$ intermediates promotes the formation of stronger Zn–O bonds, resulting in a highly ordered crystal lattice.

The high-binding-energy component observed near 533.1–533.3 eV is attributed to chemisorbed oxygen species and surface hydroxyl groups (Oads) originating from adsorbed water molecules and residual phytochemical species [44]. The gradual decrease in the Oads contribution with increasing synthesis temperature indicates progressive surface passivation and reduced adsorption-induced surface defects. This behavior agrees remarkably well with the FTIR spectra, where the significant reduction in hydroxyl-, carbonyl-, and ether-related absorption bands confirms the removal of phytochemical residues from the nanoparticle surface during hydrothermal crystallization.

The quantitative O 1s peak-area analysis summarized in **Table 6** demonstrates a systematic increase in the lattice oxygen fraction from 62.4% to 78.9%, accompanied by a substantial reduction in oxygen-vacancy concentration and surface-adsorbed oxygen species. These results clearly indicate that increasing hydrothermal temperature effectively tailors the defect chemistry and surface electronic structure of the biosynthesized ZnO nanoparticles.

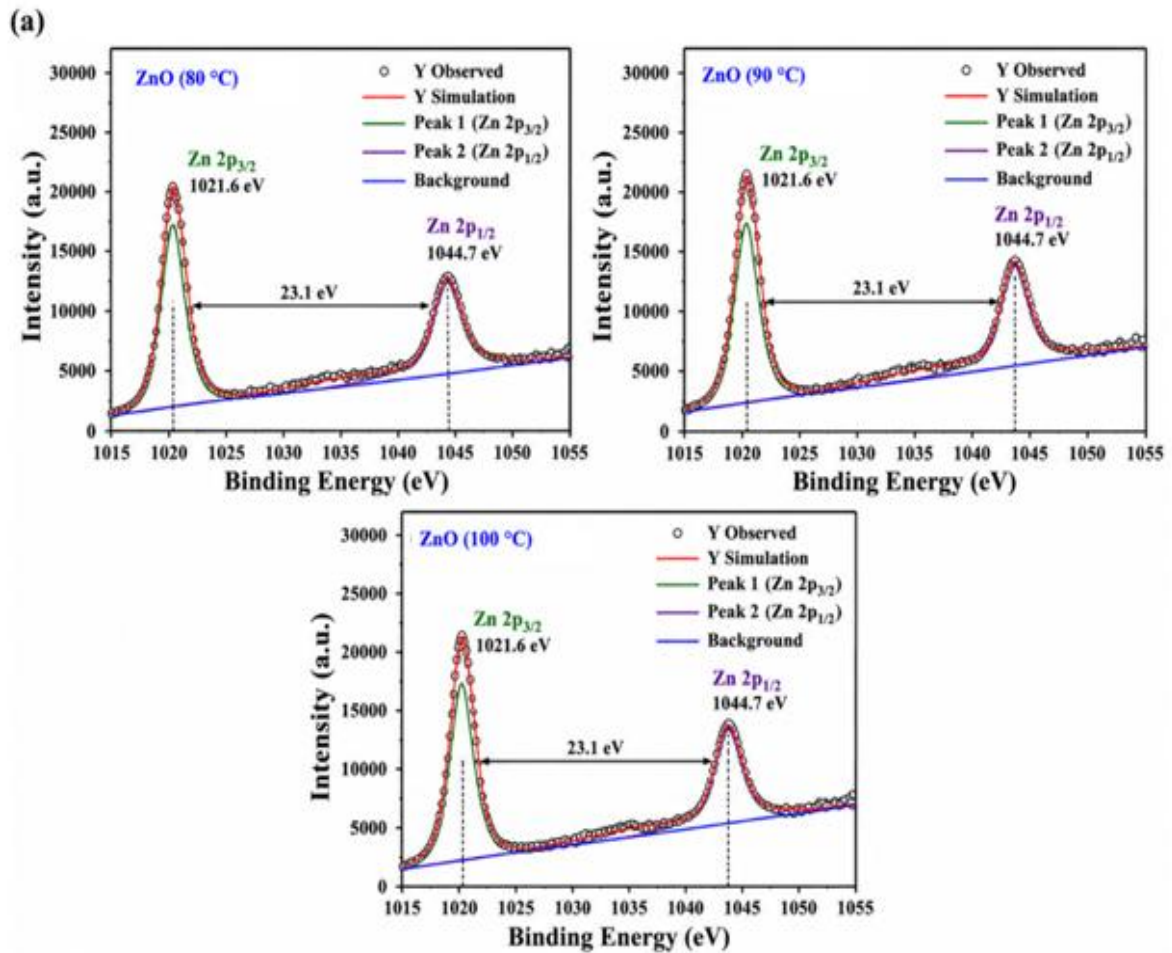
The reduction in oxygen-vacancy concentration obtained from XPS exhibits excellent agreement with the complementary characterization techniques employed in this study. The suppression of oxygen-related defects corresponds directly to the weakening of the defect-sensitive $A_1(\text{LO})/E_1(\text{LO})$ Raman mode, confirming improved lattice ordering and reduced structural disorder [45,46]. Likewise, the increased lattice oxygen fraction correlates with the enhanced crystallinity and reduced microstrain determined from XRD, the improved particle morphology observed by FESEM and TEM, and the progressive strengthening of the Zn–O framework identified by FTIR. Furthermore, the decrease in oxygen-vacancy concentration is consistent with the lower Urbach energy obtained from UV–Vis spectroscopy, indicating reduced electronic disorder near the band edges. The reduced concentration of oxygen-vacancy-related defects also explains the suppression of defect-related visible photoluminescence, demonstrating that fewer oxygen-vacancy-assisted recombination centers are present in the ZnO lattice at higher hydrothermal temperatures.

The temperature-dependent evolution of the XPS spectra also provides important insight into the role of Mahua phytochemicals during the green synthesis process. Hydroxyl-, carbonyl-, and ether-containing biomolecules initially coordinate with Zn^{2+} ions, forming Zn–organic complexes that regulate nucleation and stabilize the growing nanoparticles [47]. During hydrothermal treatment, these organic complexes progressively decompose and desorb from the nanoparticle surface, while simultaneous dehydration of $\text{Zn}(\text{OH})_2$ intermediates promotes the formation of a continuous Zn–O network. Consequently, increasing hydrothermal temperature not only removes residual phytochemical species but also enhances Zn–O bond formation, reduces oxygen-vacancy concentration, and improves surface passivation, leading to highly crystalline ZnO nanoparticles with superior structural and optical properties. The XPS investigation demonstrates that hydrothermal temperature is a decisive parameter

governing the surface chemistry, defect structure, and electronic properties of Mahua-mediated ZnO nanoparticles [48]. The excellent agreement between XPS, FTIR, XRD, FESEM, TEM, Raman, UV–Vis, and PL analyses provides compelling evidence that increasing hydrothermal temperature effectively promotes defect healing, strengthens Zn–O bonding, improves lattice ordering, and enhances the overall crystal quality of the biosynthesized ZnO nanoparticles.

Table 6: Quantitative O 1s XPS peak deconvolution showing the evolution of lattice oxygen, oxygen-vacancy-related defects, and adsorbed oxygen species with increasing hydrothermal temperature.

Sample	Lattice Oxygen, OL (%)	Oxygen Vacancy, OV (%)	Adsorbed Oxygen, Oads (%)	OL/OV Ratio
Z80 (80 °C)	62.4	26.8	10.8	2.33
Z90 (90 °C)	71.2	19.4	9.4	3.67
Z100 (100 °C)	78.9	13.5	7.6	5.84



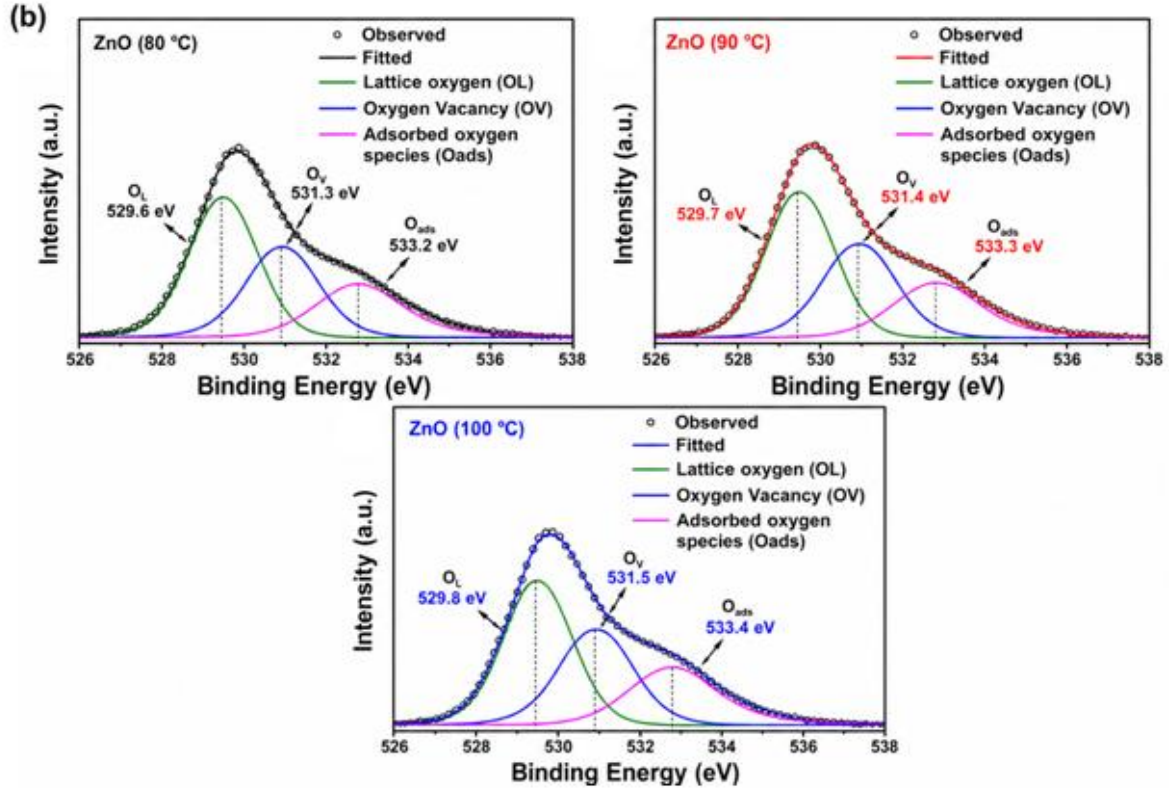


Figure 8: High-resolution XPS spectra of biosynthesized ZnO nanoparticles synthesized at hydrothermal temperatures of 80 °C (Z80), 90 °C (Z90), and 100 °C (Z100): (a) Zn 2p core-level spectra showing Zn²⁺ chemical states and (b) deconvoluted O 1s spectra resolved into lattice oxygen (OL), oxygen-vacancy-related oxygen (OV), and adsorbed oxygen species (Oads).

3.7 UV–Visible Diffuse Reflectance Spectroscopy (UV–Vis DRS)

3.7.1 Optical Band Gap Analysis

The optical properties of the biosynthesized ZnO nanoparticles were investigated using UV–visible diffuse reflectance spectroscopy (UV–Vis DRS) in the wavelength range of 200–800 nm [47–49]. Diffuse reflectance spectroscopy is a powerful technique for probing the electronic band structure of semiconductor nanomaterials and evaluating the influence of crystallinity, particle size, and defect states on their optical response [50]. The diffuse reflectance spectra together with the corresponding Tauc plots are presented in **Figure 9**, while the extracted optical band-gap values are summarized in **Table 7**.

All ZnO samples exhibit a sharp absorption edge in the near-ultraviolet region, confirming the direct electronic transition characteristic of hexagonal wurtzite ZnO. The absence of additional absorption bands in the visible region further indicates the formation of phase-pure ZnO without detectable secondary phases, in agreement with the XRD and XPS analyses [51]. The absorption edge gradually shifts toward shorter wavelengths with increasing hydrothermal temperature, indicating a progressive modification of the electronic structure as crystallization proceeds.

The optical band gap (E_g) was determined using the Tauc relation for a direct allowed semiconductor [52]:

$$(\alpha h\nu)^2 = A(h\nu - E_g)$$

where α is the absorption coefficient, $h\nu$ is the photon energy, A is a proportionality constant, and E_g is the optical band-gap energy. The band-gap values were obtained by extrapolating the linear portion of the $(\alpha h\nu)^2$ versus $h\nu$ plots to the photon-energy axis (Figure 11b). The linear fitting exhibited excellent agreement ($R^2 > 0.99$), confirming the reliability of the extracted band-gap values.

The calculated optical band gaps were 3.20 eV, 3.30 eV, and 3.41 eV for the samples synthesized at 80 °C (Z80), 90 °C (Z90), and 100 °C (Z100), respectively (Table 7). The systematic increase in band-gap energy with hydrothermal temperature is primarily attributed to improved crystallinity and progressive suppression of defect-induced localized electronic states rather than quantum confinement, since the average particle sizes determined from TEM (24.9–36.7 nm) are significantly larger than the exciton Bohr radius of ZnO (~2.3 nm). Consequently, the observed optical evolution originates predominantly from defect engineering and lattice ordering [53,54].

Increasing hydrothermal temperature enhances ionic diffusion, promotes complete dehydration of Zn(OH)_2 intermediates, and facilitates dissolution–reprecipitation during crystal growth. These processes strengthen Zn–O bonding, improve long-range lattice ordering, and suppress oxygen-vacancy-related defect states near the band edges. As a result, the density of localized electronic states decreases, leading to a widening of the optical band gap and a sharper absorption edge [55].

The optical behavior observed by UV–Vis DRS is strongly supported by the complementary characterization techniques employed in this study. The increase in band-gap energy correlates well with the larger crystallite size and reduced microstrain obtained from XRD, the improved particle morphology observed by FESEM and TEM, the enhanced Zn–O framework identified by FTIR, the stronger Raman $E_2(\text{high})$ phonon mode, and the lower oxygen-vacancy concentration determined from XPS [56]. Furthermore, the reduced density of defect states is consistent with the suppression of defect-related visible photoluminescence, demonstrating that increasing hydrothermal temperature effectively improves the electronic quality of the ZnO lattice.

The UV–Vis DRS results demonstrate that hydrothermal temperature serves as an effective parameter for tailoring the electronic structure of Mahua-mediated ZnO nanoparticles through defect healing and enhanced lattice ordering, thereby producing highly crystalline ZnO with superior optical characteristics suitable for photocatalysis, ultraviolet photodetectors, transparent optoelectronic devices, and other semiconductor-based applications [57–59].

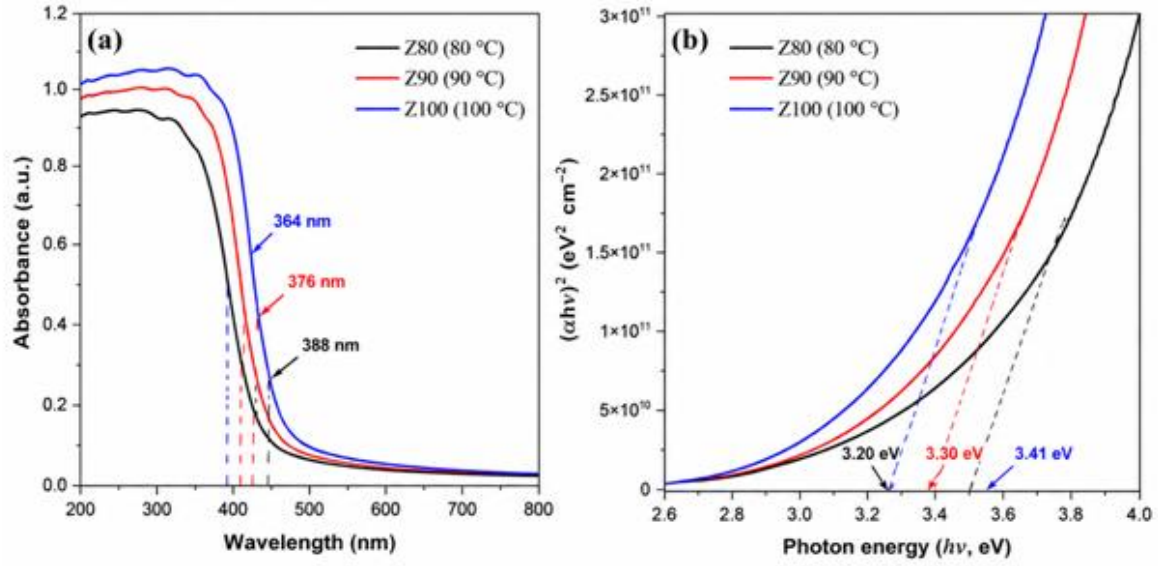


Figure 9: (a) UV–visible diffuse reflectance spectra of Mahua (*Madhuca longifolia*)-mediated ZnO nanoparticles synthesized at 80 °C (Z80), 90 °C (Z90), and 100 °C (Z100). The absorption edge progressively shifts toward shorter wavelengths with increasing hydrothermal temperature. (b) Corresponding Tauc plots $(\alpha h\nu)^2$ versus photon energy ($h\nu$) used for determining the direct optical band gap of ZnO.

Table 7: Optical band-gap parameters of biosynthesized ZnO nanoparticles synthesized at different hydrothermal temperatures.

Sample	Hydrothermal Temperature (°C)	Absorption Edge (nm)	Optical Band Gap, E_g (eV)	Linear Fit (R^2)
Z80	80	388	3.20	0.998
Z90	90	376	3.30	0.999
Z100	100	364	3.41	0.999

3.7.2 Urbach Energy Analysis

The degree of structural disorder and localized electronic states in the biosynthesized ZnO nanoparticles was further evaluated through Urbach energy (E_u) analysis. The variation of $\ln(\alpha)$ as a function of photon energy is shown in **Figure 10**, and the calculated Urbach energy values together with the corresponding structural parameters are summarized in **Table 8**.

The exponential absorption tail observed below the fundamental absorption edge arises from localized electronic states associated with lattice imperfections, oxygen vacancies, microstrain, and structural disorder. The Urbach energy was determined from the inverse slope of the linear region of the $\ln(\alpha)$ versus $h\nu$ plots according to the Urbach relation [60]:

$$\alpha = \alpha_0 \exp \frac{h\nu}{E_u}$$

where α is the absorption coefficient, α_0 is a constant, $h\nu$ is the photon energy, and E_u is the Urbach energy.

The calculated Urbach energy decreases systematically from 0.312 eV for Z80 to 0.246 eV for Z90 and 0.181 eV for Z100, indicating a progressive reduction in structural disorder with increasing hydrothermal temperature. The broad absorption tail observed for Z80 reflects a relatively high density of localized states produced by oxygen vacancies and lattice imperfections, whereas the sharper absorption edge observed for Z100 indicates a more ordered electronic structure with fewer defect-related states [61].

The reduction in Urbach energy is directly associated with the enhanced hydrothermal crystallization process. Elevated synthesis temperatures promote atomic diffusion, facilitate defect annihilation, and improve Zn–O bond formation, thereby reducing structural disorder and minimizing electronic band-tail states. Consequently, the electronic structure approaches that of an ideal crystalline semiconductor [62-66].

The Urbach-energy evolution exhibits excellent agreement with all complementary characterization techniques employed in this work. The lower E_u values correlate with the increased crystallite size and reduced lattice strain obtained from XRD, the improved particle morphology observed by FESEM and TEM, the strengthening of the Zn–O framework identified by FTIR, the enhancement of the Raman $E_2(\text{high})$ mode, the significant reduction in oxygen-vacancy concentration determined by XPS, and the suppression of defect-related visible photoluminescence [67,68]. These complementary observations consistently demonstrate that increasing hydrothermal temperature effectively heals structural defects and improves both lattice ordering and electronic quality.

A clear inverse relationship between Urbach energy and crystallite size is observed, whereas a direct relationship exists between Urbach energy and oxygen-vacancy concentration. This behavior confirms that the electronic disorder in Mahua-mediated ZnO nanoparticles is predominantly governed by intrinsic lattice defects rather than particle-size effects.

The combined UV–Vis DRS and Urbach-energy analyses establish a comprehensive structure–property relationship, demonstrating that increasing hydrothermal temperature simultaneously enhances crystallinity, suppresses oxygen-vacancy-related defect states, strengthens Zn–O bonding, and improves the optical quality of biosynthesized ZnO nanoparticles.

Table 8: Correlation between structural and optical parameters of biosynthesized ZnO nanoparticles synthesized at different hydrothermal temperatures.

Sample	Crystallite Size (nm)	Optical Band Gap (eV)	Urbach Energy (eV)	Oxygen Vacancy (%)	Microstrain ($\times 10^{-3}$)
Z80	24.9	3.20	0.312	26.8	4.67
Z90	28.1	3.30	0.246	19.4	3.86
Z100	36.7	3.41	0.181	13.5	3.19

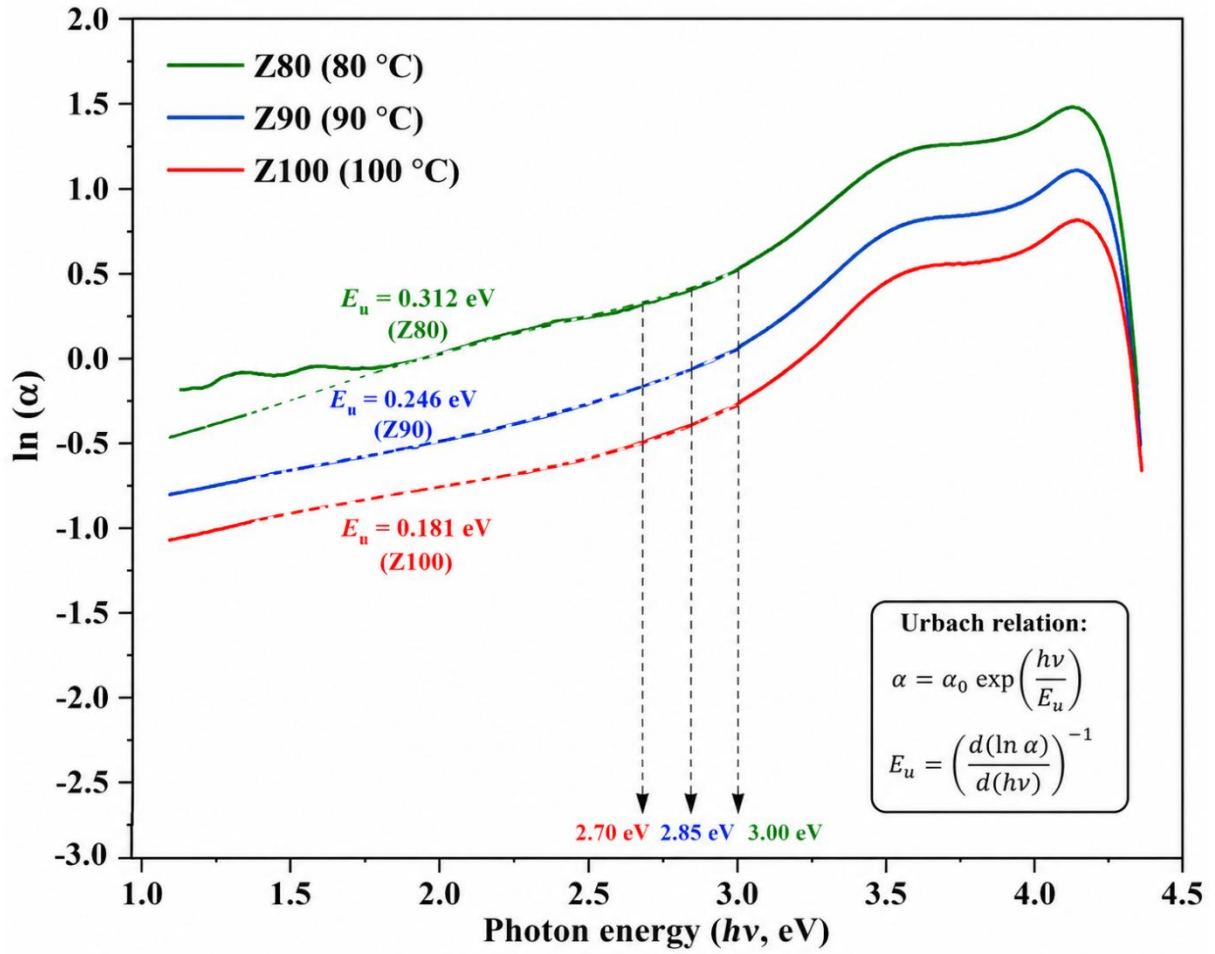


Figure 10: Urbach energy analysis of Mahua-mediated ZnO nanoparticles synthesized at 80 °C (Z80), 90 °C (Z90), and 100 °C (Z100).

3.8 Photoluminescence (PL) Characteristics

Photoluminescence (PL) spectroscopy was employed to investigate the defect-related optical emission and charge-carrier recombination behavior of the Mahua-mediated ZnO nanoparticles synthesized at different hydrothermal temperatures [69]. The PL spectra recorded under near-ultraviolet excitation (330 nm) are presented in Figure 11. All samples exhibit a broad visible emission band extending from approximately 450 to 700 nm, with a dominant green emission centered at ~537 nm, indicating that the luminescence is primarily governed by intrinsic defect states rather than near-band-edge (NBE) excitonic recombination.

In ZnO, ultraviolet NBE emission originates from the radiative recombination of free excitons, whereas the broad visible emission arises from intrinsic lattice defects. In the present study, the NBE emission is weak and poorly resolved, while the defect-related visible emission dominates the spectra, suggesting that intrinsic defects play a major role in the radiative recombination process of the biosynthesized nanoparticles. The dominant green emission centered at ~537 nm is attributed mainly to oxygen-vacancy-related defect states (V_o), which introduce localized donor levels within the band gap. Electrons trapped at these

defect levels recombine radiatively with holes in the valence band, giving rise to the characteristic green luminescence.

A pronounced dependence of the PL intensity on hydrothermal synthesis temperature is observed [70,71]. The Z80 sample exhibits the highest green emission intensity, indicating the presence of a relatively high concentration of oxygen vacancies and structural imperfections. As the synthesis temperature increases to 90 °C and 100 °C, the intensity of the green emission decreases progressively, demonstrating a substantial reduction in defect-assisted radiative recombination. This behavior indicates that elevated hydrothermal temperatures effectively suppress the formation of intrinsic lattice defects while improving the structural quality of the ZnO nanoparticles.

The reduction in defect-related PL intensity can be explained by the temperature-dependent hydrothermal crystallization mechanism [72]. At lower synthesis temperatures, rapid nucleation produces a large number of nanocrystals containing oxygen-deficient regions, lattice distortions, and unsaturated surface bonds, which act as efficient radiative recombination centers. Increasing the hydrothermal temperature enhances atomic diffusion, dissolution–reprecipitation, and crystal growth, enabling Zn and O atoms to occupy thermodynamically stable lattice positions. Consequently, oxygen vacancies are progressively healed, lattice disorder decreases, and defect-mediated recombination is significantly suppressed, leading to lower visible PL intensity.

The PL results exhibit excellent agreement with the complementary structural and spectroscopic analyses. The gradual suppression of the green emission closely follows the decrease in oxygen-vacancy concentration determined from XPS O 1s analysis, where the defect fraction decreases systematically from 26.8% (Z80) to 19.4% (Z90) and 13.5% (Z100). Similarly, the weakening of the defect-sensitive $A_1(LO)/E_1(LO)$ Raman mode confirms the reduction of oxygen-vacancy-related lattice defects with increasing hydrothermal temperature. The improved crystallinity revealed by XRD, including increased crystallite size and reduced microstrain, together with the well-defined particle morphology observed by FESEM and TEM, further supports the progressive enhancement of lattice ordering.

Moreover, the PL behavior correlates closely with the FTIR results, where the gradual disappearance of hydroxyl-, carbonyl-, and ether-containing phytochemical residues together with the strengthening of the Zn–O stretching vibration confirms the formation of a more complete Zn–O network and reduced surface defect density [73]. A similar trend is observed in the optical absorption analysis, where the Urbach energy decreases from 0.312 eV to 0.181 eV with increasing synthesis temperature, indicating suppression of localized electronic states and reduced structural disorder. The simultaneous reduction in Urbach energy and defect-related PL emission confirms that hydrothermal treatment effectively minimizes defect-induced band-tail states and improves the electronic quality of the ZnO nanoparticles.

The PL investigation demonstrates that hydrothermal temperature plays a decisive role in tailoring the defect chemistry and optical emission behavior of Mahua-mediated ZnO nanoparticles [74]. The excellent agreement between PL, XPS, Raman, XRD, FTIR, FESEM, TEM, and UV–Vis analyses provides compelling evidence that increasing hydrothermal temperature promotes defect healing, strengthens the Zn–O framework, suppresses oxygen-vacancy-assisted radiative recombination, and significantly enhances the structural and optical quality of the biosynthesized ZnO nanoparticles.

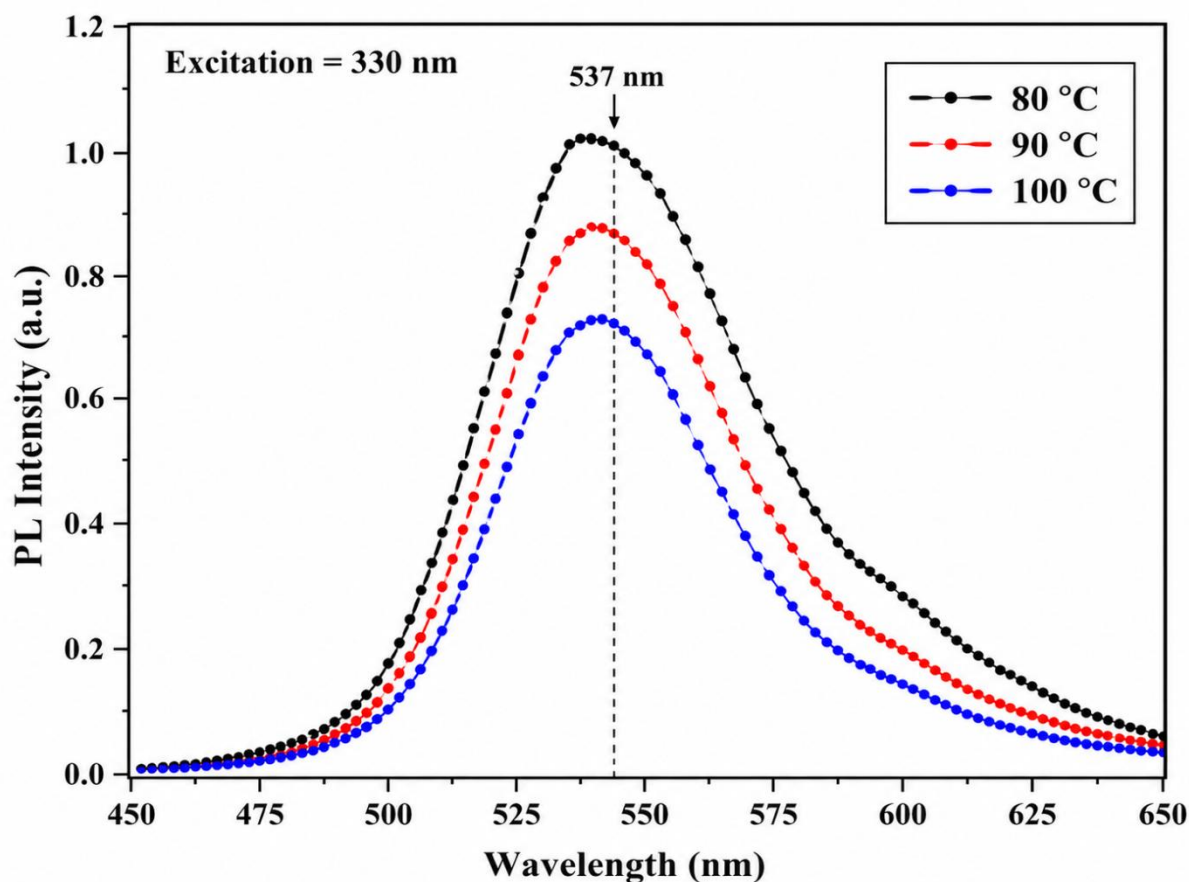


Figure 11: Photoluminescence spectra of Mahua-mediated ZnO nanoparticles synthesized at 80 °C (Z80), 90 °C (Z90), and 100 °C (Z100) under 330 nm excitation.

3.8.1 Defect-Mediated Photoluminescence Mechanism

The defect-mediated photoluminescence mechanism of the biosynthesized ZnO nanoparticles is schematically illustrated in Figure 12. Under 330 nm near-ultraviolet excitation, electrons are excited from the valence band (VB) to the conduction band (CB), generating electron–hole pairs. While direct band-edge recombination can produce ultraviolet emission, the presence of intrinsic oxygen-vacancy (V_o) defects introduces localized donor states within the band gap that dominate the recombination process [75].

Following photoexcitation, a fraction of the excited electrons is captured by oxygen-vacancy-related defect levels before undergoing radiative recombination with holes in the valence band. This defect-assisted transition produces the broad green emission centered at approximately 537 nm, which represents the dominant luminescence observed experimentally. The intensity of this emission is therefore directly related to the concentration of oxygen-vacancy defects within the ZnO lattice.

Increasing the hydrothermal synthesis temperature reduces the density of oxygen-vacancy defects through enhanced crystallization, improved atomic diffusion, and the formation of a more ordered Zn–O network. Consequently, fewer defect states are available for carrier trapping, resulting in weaker defect-mediated green emission and improved optical quality. This mechanism is fully consistent with the quantitative XPS analysis showing reduced oxygen-vacancy concentration, the weakening of the Raman LO defect mode, the decrease in Urbach energy, and the improved crystallinity determined from XRD.

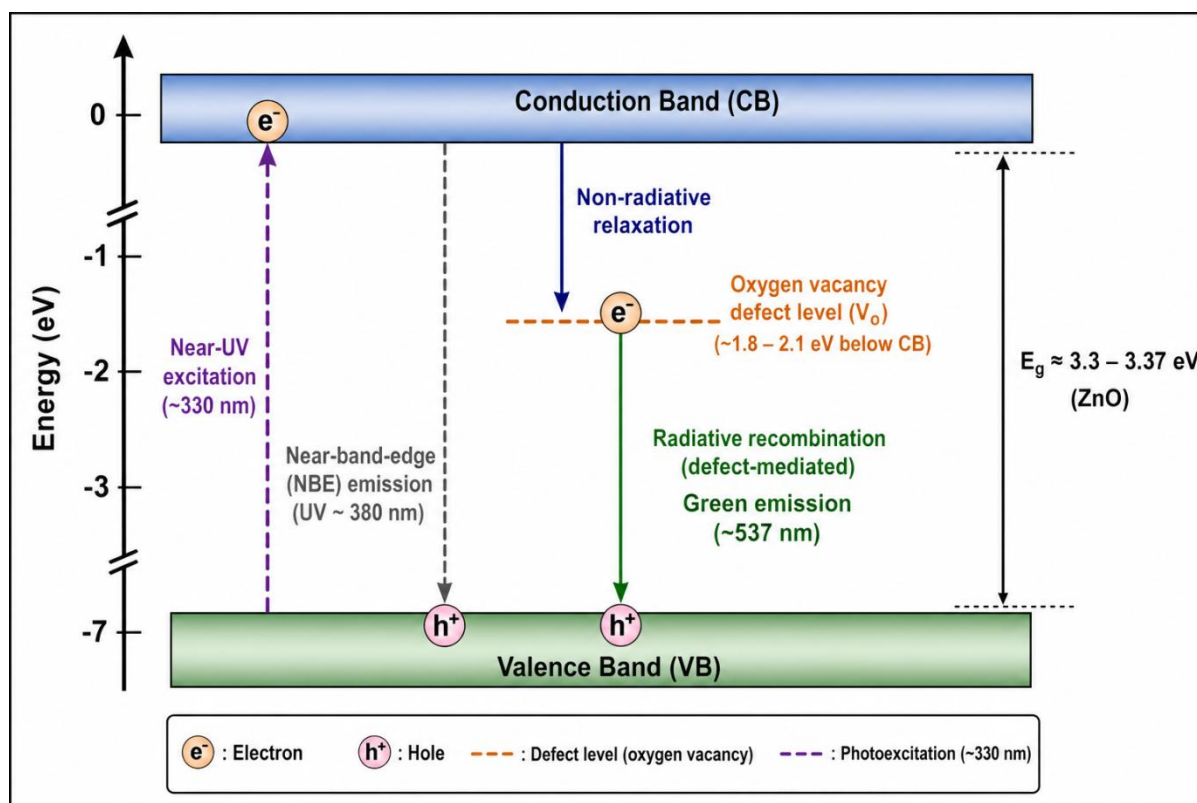


Figure 12: Schematic illustration of the defect-mediated photoluminescence mechanism in Mahua-mediated ZnO nanoparticles.

5. Conclusion

In this work, phase-pure ZnO nanoparticles were successfully synthesized through a sustainable phytochemical-assisted hydrothermal route using *Madhuca longifolia* (Mahua) flower extract without any post-calcination treatment. The influence of hydrothermal temperature (80–100 °C) on the structural evolution, defect chemistry, morphology, and optical properties of the biosynthesized ZnO nanoparticles was systematically investigated using complementary characterization techniques.

XRD analysis confirmed the formation of single-phase hexagonal wurtzite ZnO with progressively improved crystallinity as the synthesis temperature increased. The crystallite size increased from 24.9 to 36.7 nm, accompanied by a significant reduction in lattice microstrain and dislocation density, demonstrating enhanced crystal growth and structural ordering. FESEM and TEM analyses revealed a systematic morphological evolution from agglomerated quasi-spherical nanoparticles to well-defined rod-like nanostructures with improved particle uniformity. FTIR spectroscopy indicated the participation of hydroxyl-,

carbonyl-, and ether-containing phytochemicals during nanoparticle formation, while the gradual removal of residual organic species at higher hydrothermal temperatures promoted the formation of a stronger Zn–O framework. Raman spectroscopy further confirmed enhanced lattice ordering through the progressive sharpening of the characteristic $E_2(\text{high})$ phonon mode and suppression of the defect-related $A_1(\text{LO})/E_1(\text{LO})$ mode. Quantitative XPS analysis revealed a systematic decrease in oxygen-vacancy concentration from 26.8% to 13.5%, demonstrating effective defect engineering under mild hydrothermal conditions. UV–Vis diffuse reflectance spectroscopy showed a systematic increase in the optical band gap from 3.20 to 3.41 eV, accompanied by a reduction in Urbach energy from 0.312 to 0.181 eV, indicating suppression of electronic disorder and localized defect states. The progressive reduction in defect-related green photoluminescence further corroborated the improved structural quality and reduced oxygen-vacancy-assisted radiative recombination. The excellent agreement among XRD, FESEM, TEM, FTIR, Raman, XPS, UV–Vis, and PL analyses establishes a clear structure–defect–property relationship governed by hydrothermal temperature.

Overall, this study demonstrates that phytochemical-assisted low-temperature hydrothermal synthesis is an effective and environmentally sustainable strategy for tailoring the crystallinity, defect chemistry, and optical properties of ZnO nanoparticles without the need for high-temperature calcination. The ability to obtain highly crystalline ZnO at temperatures as low as 80–100 °C provides an energy-efficient alternative to conventional synthesis methods and highlights the potential of Mahua-mediated ZnO nanostructures for future applications in photocatalysis, ultraviolet photodetectors, optoelectronic devices, gas sensors, and other semiconductor-based technologies.

Limitation

Despite these promising findings, several limitations should be acknowledged. The present work did not include a control synthesis in the absence of *Madhuca longifolia* extract; therefore, the specific contribution of individual phytochemical constituents to nucleation, crystal growth, and defect regulation could not be experimentally isolated. In addition, the proposed growth mechanism is inferred from the observed structural evolution and previously reported literature rather than direct phytochemical characterization. Furthermore, although the structural and optical properties indicate significant potential for functional applications, practical performance evaluations such as photocatalytic degradation, photoelectrochemical response, gas sensing, or antibacterial activity were beyond the scope of the present investigation.

Future Work

Future studies should therefore focus on performing comparative control experiments, comprehensive phytochemical characterization using techniques such as GC–MS or LC–MS, and advanced defect investigations through complementary methods including electron paramagnetic resonance (EPR) spectroscopy. Evaluating the photocatalytic, photoelectrochemical, sensing, and antimicrobial performance of the optimized ZnO nanoparticles will further establish the relationship between defect engineering and functional properties. Such investigations will provide deeper mechanistic insight into phytochemical-assisted crystallization and facilitate the rational design of sustainable, high-performance ZnO nanomaterials for advanced environmental and optoelectronic applications.

Declaration

Availability of Data and Materials

All data generated or analyzed during this study are included in this published article and its supplementary material. Further details can be made available from the corresponding author upon reasonable request.

AI Declaration

AI-assisted tools were used solely for language editing, grammar correction, and manuscript polishing. All scientific content, experimental design, data interpretation, and conclusions were independently performed and verified by the authors.

Competing Interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Funding

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

Authors' Contributions

Dr. Dipti Shukla conceptualized the research idea and supervised the experimental work. The synthesis and characterization were performed. Data analysis, interpretation, and manuscript drafting were primarily carried out by Dr. Dipti Shukla. All authors reviewed and approved the final manuscript.

Acknowledgements

The authors acknowledge the Department of Physics, OPJU Raigarh, for providing laboratory facilities and research support. The authors also thank colleagues and technical staff for their assistance during experimental work and data analysis.

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