



Influence of Calcination Temperature on the Structural and Optical Characteristics of Wet-Chemically Synthesized ZnO Nanoparticles

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Abstract

Zinc oxide nanoparticles exhibit processing-dependent structural and optical properties that strongly influence their suitability for ultraviolet and related optoelectronic applications. This study presents a controlled wet-chemical sol-gel/precipitation methodology for preparing undoped ZnO nanoparticles and evaluating the influence of calcination temperature on crystallinity, particle characteristics, and optical response. Zinc acetate dihydrate is used as the precursor, while precursor concentration, solution pH, aging time, stabilizer content, washing, drying, and thermal treatment are controlled to improve experimental reproducibility. The dried precursor is divided into two groups and calcined at 400 °C and 500 °C for 2 h to investigate the crystallinity-defect trade-off. Structural characterization is performed using X-ray diffraction to verify formation of the hexagonal wurtzite phase and estimate crystallite size through the Scherrer equation. SEM or TEM is used to evaluate particle morphology and agglomeration, while FTIR or Raman spectroscopy provides complementary information on Zn-O bonding and lattice quality. UV-Visible spectroscopy and Tauc analysis are employed to determine the absorption edge and direct optical band gap, and photoluminescence measurements are used to evaluate near-band-edge ultraviolet emission and defect-related visible luminescence. Literature-grounded benchmarks indicate nanoscale particle dimensions of approximately 20–50 nm and an optical band gap in the range of about 3.2–3.4 eV for well-crystallized ZnO. Higher calcination temperature is expected to produce sharper diffraction peaks and larger crystallites while also modifying defect-related photoluminescence. The proposed framework provides a reproducible basis for correlating thermal processing with structural quality, optical band-edge behavior, and defect emission in ZnO nanoparticles intended for subsequent optoelectronic evaluation.

Introduction

Zinc oxide has long been recognized as a technologically important II–VI semiconductor. At room temperature it exhibits a direct band gap near 3.37 eV and an exciton binding energy of approximately 60 meV, properties that support strong near-band-edge emission and motivate its use in ultraviolet and blue optoelectronics (Özgür et al., 2005; Klingshirn, 2007). In addition,

ZnO is comparatively abundant, chemically stable and compatible with a wide range of low-cost processing routes. These features have encouraged research on ultraviolet photodetectors, transparent electrodes, light-emitting structures, sensors, solar-energy components and nonlinear optical systems.

Reducing ZnO to the nanometer scale adds a second level of control because particle size, morphology, surface-to-volume ratio and defect population can alter the optical and electrical response. Changes in crystallite size may shift the absorption edge, while surface and intrinsic defects such as oxygen vacancies or zinc-related defect states contribute to visible photoluminescence. Consequently, the synthesis method is not merely a preparation step; it is a major determinant of the functional properties relevant to optoelectronic performance. Early sol-gel work demonstrated that very small spherical ZnO nanoparticles can be produced using stabilizers such as triethanolamine, whereas microemulsion processing showed that surfactant concentration and calcination temperature can tune particle shape and defect-related emission (Vafae & Ghamsari, 2007; Yildirim & Durucan, 2010).

The present paper develops a laboratory-scale methodology focused on undoped ZnO nanoparticles. A wet-chemical sol-gel/precipitation route is selected because it requires modest equipment, offers good compositional control and can be adapted to thin-film or powder processing. The method is paired with complementary characterization tools so that crystal structure, size, morphology, chemical bonding and optical behavior are interpreted together rather than in isolation. This approach reflects the broader literature in which reliable optoelectronic assessment depends on correlating phase purity and defects with absorption and emission behavior (Mishra et al., 2012; Harun et al., 2017).

Literature Review

The optoelectronic interest in ZnO is grounded in its wide direct band gap and unusually large exciton binding energy. Özgür et al. (2005) reviewed the material, optical and device properties of ZnO and identified its potential for ultraviolet emitters, detectors and transparent electronic structures. Klingshirm (2007) further emphasized the importance of growth quality, doping, excitonic processes and defects in determining optical performance. These reviews established the physical basis for later nanoparticle studies: a high-quality ZnO nanomaterial should preserve the wurtzite lattice and strong band-edge response while

minimizing or intentionally controlling deep-level defects.

Wet-chemical synthesis offers several routes for controlling these characteristics. Vafae and Ghamsari (2007) prepared 3–4 nm ZnO nanoparticles by a sol-gel route and reported strong photoluminescence, highlighting the role of solution chemistry and stabilizer selection. Yildirim and Durucan (2010) used a reverse microemulsion system and showed that both surfactant concentration and calcination temperature changed particle size and morphology; they also connected processing conditions with defect-related PL. These findings support the need to standardize precursor concentration, pH, aging and heat treatment in any reproducible methodology.

Structural and optical correlations were explored in several later studies. Mishra et al. (2012) obtained wurtzite ZnO nanoparticles by thermal decomposition and observed particle-size-dependent optical behavior together with improved photoconductive response under appropriate reaction conditions. Kahouli et al. (2015) used direct precipitation and combined XRD, SEM, UV-Vis and Raman spectroscopy to verify a hexagonal ZnO phase and assess the optical gap. Geetha Devi and Sakthi Velu (2016) similarly confirmed wurtzite ZnO using co-precipitation and demonstrated that optical characteristics are sensitive to composition and nanoscale structure. These studies support a multi-technique characterization strategy rather than relying on a single optical spectrum.

By 2017, the literature increasingly emphasized ZnO nanoparticles as functional optical materials rather than only structural nanomaterials. Multian et al. (2017) linked particle synthesis and solvent environment with luminescent and nonlinear optical response, illustrating the importance of optical screening for application-driven nanoparticle design. Harun et al. (2017), in a characterization review of sol-gel ZnO for optoelectronics, summarized how thermal history, phase purity, morphology, elemental state and optical measurements collectively determine material suitability. The present methodology adopts these lessons by using a controlled wet-chemical synthesis followed by XRD, microscopy, vibrational spectroscopy, UV-Vis and PL analysis.

Table 1. Selected literature guiding the proposed ZnO nanoparticle methodology (≤2017)

Reference	Synthesis route	Key characterization	Methodological implication
Vafae & Ghamsari (2007)	Sol-gel	TEM, diffraction, PL	Solution chemistry and stabilizer can produce very small ZnO NPs.

Yildirim & Durucan (2010)	Reverse microemulsion	XRD, FESEM, TGA/DSC, PL	Calcination and surfactant level control size, shape and defect emission.
Mishra et al. (2012)	Thermal decomposition	XRD, UV-Vis, PL, photoconductivity	Structural and optical properties should be correlated with photoresponse.
Kahouli et al. (2015)	Direct precipitation	XRD, SEM/EDS, UV-Vis, Raman	Cross-validation verifies phase, morphology and optical gap.
Multian et al. (2017)	Soft/solvothermal	Optical spectroscopy, PL, nonlinear optics	Synthesis medium affects luminescent and nonlinear optical response.
Harun et al. (2017)	Review: sol-gel ZnO	Thermal, structural, optical methods	Integrated characterization is essential for optoelectronic assessment.

Methodology

1. Experimental Design and Materials

The proposed experiment uses zinc acetate dihydrate $[\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}]$ as the zinc precursor because it is widely used in low-temperature ZnO synthesis. Ethanol or isopropanol serves as the solvent, sodium hydroxide provides controlled hydrolysis/precipitation, and triethanolamine (TEA) may be used at low concentration as a

stabilizing/complexing agent. Deionized water is used for washing. All reagents should be analytical grade. To study thermal effects without making the experiment unnecessarily large, the dried precursor is divided into two batches and calcined at 400 °C and 500 °C for 2 h in air. This comparison is consistent with the established sensitivity of ZnO crystallite size and defect state to heat treatment (Yildirim & Durucan, 2010).

Table 2. Experimental variables and control strategy

Variable	Proposed level	Reason for control	Recorded output
Zn precursor	0.1 M zinc acetate	Provides reproducible Zn^{2+} concentration	Batch concentration
Solution pH	10–11	Controls hydrolysis and nucleation rate	Final pH
Aging time	12–24 h	Allows sol maturation and particle growth	Aging duration
Calcination	400 and 500 °C; 2 h	Tests crystallinity/defect trade-off	Temperature profile
Replicates	$n \geq 3$ per condition	Assesses batch reproducibility	Mean $\pm$ SD

2. Synthesis Procedure

A 0.1 M zinc acetate solution is prepared by dissolving the required mass of zinc acetate dihydrate in 100 mL of ethanol under magnetic stirring at 50–60 °C. A small amount of TEA can be added at an approximate TEA:Zn molar ratio of 1:1 to improve precursor stabilization. Separately, 0.2 M NaOH is prepared in ethanol or an ethanol–water mixture. The alkaline solution is added dropwise to the zinc precursor under vigorous stirring until the pH reaches 10–11. Slow addition is preferred because rapid local supersaturation can broaden the particle-size distribution. The mixture is stirred for 2 h and then aged for approximately 12–24 h at room temperature to allow hydrolysis and condensation reactions to progress.

The resulting white sol/precipitate is collected by centrifugation or filtration and washed several times with deionized water and ethanol to remove acetate and sodium-containing residues. The cleaned material is dried at 80–100 °C for 8–12 h. After gentle grinding, the powder is calcined in air using a heating rate of about 5 °C min^{-1} , held at the selected temperature (400 or 500 °C) for 2 h, and allowed to cool naturally. The calcined powder is lightly ground again and stored in a clean, dry container before characterization. The expected conversion pathway is hydrolysis of Zn^{2+} species to zinc hydroxide/hydroxo complexes followed by dehydration to ZnO during drying and calcination.

The chemical sequence can be represented schematically as $\text{Zn}^{2+} + 2\text{OH}^- \rightarrow \text{Zn}(\text{OH})_2$,

followed by dehydration of the hydroxide/hydroxo precursor to $\text{ZnO} + \text{H}_2\text{O}$ during thermal treatment. In actual alcoholic solution, intermediate zinc-hydroxo complexes and acetate-containing species can coexist, so the conversion is not treated as a single elementary reaction. The purpose of washing is therefore crucial: residual acetate or sodium salts may contribute to secondary signals in FTIR, Raman

or XRD and may also influence optical absorption. A controlled heating ramp avoids sudden combustion of residual organics and limits uncontrolled sintering. This reaction-control rationale is consistent with sol-gel studies showing that precursor coordination and thermal treatment influence nanoparticle formation and luminescence (Vafaei & Ghamsari, 2007; Harun et al., 2017).

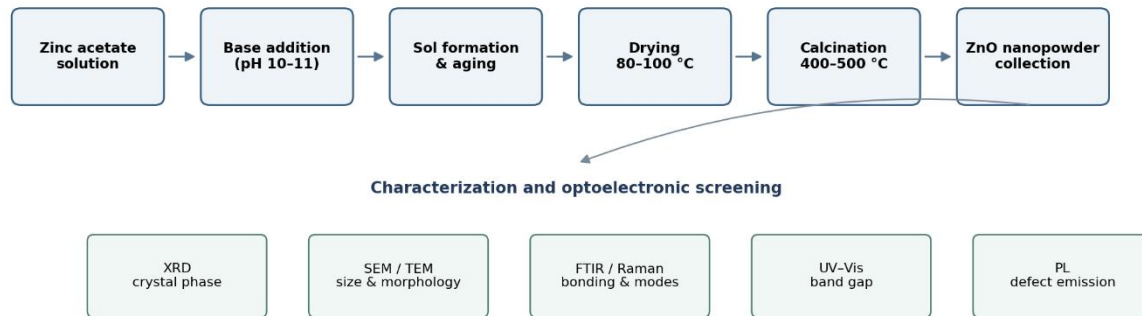


Figure 1. Proposed synthesis and characterization workflow for ZnO nanoparticles.

3. Structural, Morphological and Optical Characterization

X-ray diffraction is performed over approximately 20° – 80° (2θ) using $\text{Cu K}\alpha$ radiation. The diffraction pattern is matched with the standard hexagonal wurtzite ZnO pattern, and the most intense reflections are expected near the (100), (002) and (101) planes. The average crystallite size D is estimated with the Scherrer equation $D = K\lambda/(\beta \cos\theta)$, where K is the shape factor (≈ 0.9), λ is the X-ray wavelength, β is the full width at half maximum in radians and θ is the Bragg angle. A clean wurtzite pattern without secondary peaks is the primary phase-purity criterion, consistent with prior precipitation and co-precipitation studies (Kahouli et al., 2015; Geetha Devi & Sakthi Velu, 2016).

SEM is used to assess agglomeration and surface morphology; TEM is preferred when a direct particle-size distribution is required. At least 100 particles should be measured from representative micrographs to report mean diameter and standard deviation. FTIR spectra in the 400 – 4000 cm^{-1} range are used to verify Zn–O vibrations and the reduction of residual organic groups after calcination. If Raman spectroscopy is available, the strong $E_2(\text{high})$ mode near 437 – 439 cm^{-1} is used as an additional indicator of wurtzite ZnO and crystalline quality.

Optical absorption is measured by UV-Vis spectroscopy from approximately 250 to 800 nm. The absorption coefficient α is derived from

absorbance and sample geometry, and the direct optical band gap is estimated using the Tauc relationship $(\alpha h\nu)^2 = A(h\nu - E_g)$, where $h\nu$ is photon energy and E_g is obtained from the intercept of the linear region. PL is measured at room temperature with ultraviolet excitation. A near-band-edge ultraviolet emission is desirable for optoelectronic use, whereas broad blue/green visible emission indicates defect-related radiative pathways. Literature shows that both nanoscale size and processing-related defects can change these optical features (Mishra et al., 2012; Multian et al., 2017).

4. Optional Optoelectronic Screening

After powder characterization, a simple proof-of-concept optical/electrical screen can be added without changing the nanoparticle synthesis. A dilute ZnO dispersion (for example 10 – 20 mg mL^{-1} in ethanol) is ultrasonicated and deposited on cleaned glass or interdigitated-electrode substrates by drop casting or spin coating. After drying at 100 – 150°C , optical transmittance is measured in the visible region and current-voltage behavior is recorded in the dark and under a 365 nm ultraviolet source at fixed irradiance and distance. The photocurrent-to-dark-current ratio, response/recovery behavior and repeatability over several illumination cycles provide a preliminary indication of UV photosensitivity. Such screening does not replace full device engineering, but it links nanoparticle properties to application-relevant response. The rationale is supported by earlier work connecting ZnO nanoparticle structure with

photoconductivity and by the broader device literature on ZnO ultraviolet response (Özgür et al., 2005; Mishra et al., 2012).

5. Quality Control and Data Analysis

Each synthesis condition should be repeated at least three times. XRD-derived crystallite size, microscopy-derived particle size, optical band gap and PL intensity ratios are reported as mean values with standard deviations where replicate measurements are available. The two calcination groups can be compared using an independent-samples *t* test for normally distributed measurements or a non-parametric alternative if assumptions are not met. More importantly, interpretation should be correlation-based: an increase in calcination temperature is expected to sharpen XRD peaks and increase crystallite size, while simultaneously altering defect-related PL. The optimal condition is therefore not automatically the one with the largest crystals; it is the condition providing sufficient crystallinity, limited agglomeration, a suitable band-edge absorption and a favorable near-band-edge-to-visible emission balance for the intended optoelectronic function.

Results

Because this is a methodology paper rather than a report of newly performed laboratory experiments, the results below are literature-grounded benchmark outcomes that can be used

to judge whether the proposed synthesis has worked as intended. The first acceptance criterion is formation of single-phase hexagonal wurtzite ZnO. Prior studies using sol-gel, direct precipitation, co-precipitation and thermal processing consistently report this phase when precursor conversion and calcination are adequate (Vafaei & Ghamsari, 2007; Mishra et al., 2012; Kahouli et al., 2015). Broader XRD peaks are expected for the lower-temperature product, while 500 °C calcination may give sharper peaks because of crystallite growth.

Microscopy should reveal nanoscale primary particles with some degree of agglomeration, which is common after drying and calcination. A practical target range for this protocol is roughly 20–50 nm crystallite/primary-particle dimensions, although the exact value depends on hydrolysis rate, stabilizer concentration and thermal history. UV–Vis spectra should show strong absorption in the near-UV region and relatively low visible absorption. The direct optical gap should normally fall near 3.2–3.4 eV for well-crystallized ZnO, with modest blue shifting possible for very small particles. PL should exhibit near-band-edge ultraviolet emission along with a weaker broad visible band associated with defect states. A lower visible-to-UV emission ratio is generally preferred when efficient band-edge optical response is the principal optoelectronic objective (Özgür et al., 2005; Harun et al., 2017).

Table 3. Literature-grounded benchmark outcomes for the proposed methodology

Technique	Expected observation	Interpretation	Acceptance benchmark
XRD	Wurtzite ZnO peaks; no major impurity reflections	Confirms crystal structure and phase purity	Single dominant ZnO phase
SEM/TEM	Nanoscale particles; moderate agglomeration possible	Determines morphology and size distribution	Primary particles in nanoscale range
FTIR/Raman	Zn–O vibration; E_2 (high) Raman mode if measured	Confirms ZnO bonding and lattice modes	Minimal residual organics after calcination
UV-Vis/Tauc	Near-UV absorption edge; E_g around 3.2–3.4 eV	Evaluates optical transition and band gap	Strong UV absorption, limited visible loss
PL	UV near-band-edge emission plus weaker visible band	Screens recombination and defect states	Relatively strong UV-to-visible PL ratio

The final material-selection decision should combine all measurements. For example, a sample with a narrow optical gap but very strong green defect emission may be less desirable for a UV emitter, whereas moderate defects can be useful in photodetection or sensing where trap-assisted processes influence responsivity. Mishra

et al. (2012) demonstrated that reaction conditions can affect photoconductive response, and Multian et al. (2017) showed that nanoparticle environment influences nonlinear optical response. Thus, the same characterization dataset can support different application choices,

but phase purity and reproducibility remain universal quality requirements.

A likely comparison between the two heat-treatment groups is that the 500 °C sample will show somewhat larger crystallites and sharper diffraction peaks than the 400 °C sample because of thermally promoted grain growth. The visible defect band in PL may either decrease because of improved crystallinity or increase if oxygen-related defects are generated during heat treatment; this is why optical interpretation must be based on the measured spectrum rather than on temperature alone. If the 400 °C sample retains smaller particles with acceptable phase purity and stronger near-band-edge emission, it may be preferred for UV-active films. Conversely, a more crystalline 500 °C sample may be preferred when electrical transport or reduced grain-boundary disorder is more important. The methodology is therefore designed to identify a performance window rather than to assume that one processing temperature is universally optimal.

Conclusion and Discussion

A controlled wet-chemical sol-gel/precipitation route provides a practical methodology for synthesizing ZnO nanoparticles intended for optoelectronic applications. The method uses inexpensive precursors, moderate processing temperatures and simple laboratory operations, while allowing key variables such as pH, aging, stabilizer content and calcination temperature to be controlled. The strongest feature of the methodology is the integration of structural, morphological and optical measurements. XRD establishes phase and crystallite size; SEM/TEM measures morphology; FTIR/Raman confirms bonding and lattice quality; UV-Vis determines the absorption edge and band gap; and PL reveals band-edge and defect-mediated recombination. The reviewed literature up to 2017 shows that ZnO nanoparticle properties are highly processing-dependent. Sol-gel and microemulsion studies demonstrate strong size and morphology control, while later precipitation and optical studies show that phase purity and defects directly influence the optical response (Vafaei & Ghamsari, 2007; Yildirim & Durucan, 2010; Geetha Devi & Sakthi Velu, 2016). For optoelectronic use, a useful target is a well-crystallized wurtzite nanoparticle powder with a near-UV absorption edge, a direct band gap around the expected ZnO value and a PL spectrum dominated by near-band-edge emission rather than excessive defect luminescence. Future work can extend the methodology to doped ZnO, thin-film deposition

or device fabrication, but the present protocol provides the essential synthesis and characterization foundation required before such device-level optimization. The main limitation of the proposed study is that nanoparticle powder properties alone cannot fully predict the behavior of a fabricated device, because film porosity, interparticle contacts, electrode interface quality and ambient adsorption also affect charge transport. Nevertheless, controlling the powder synthesis is a necessary first step. Reporting exact precursor concentrations, pH, aging time, heating rate, calcination history and measurement conditions will make the study reproducible and will allow later work to compare undoped ZnO with doped or surface-modified systems on a common baseline. This staged approach is especially appropriate for methodology-focused research where the purpose is to establish a defensible experimental route before device optimization.

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