



Synthesis and Structural Characterization of Zinc Oxide Nanoparticles for Optoelectronic

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Abstract

Zinc oxide (ZnO) is a direct wide-band-gap semiconductor whose nanoscale form combines chemical stability, optical transparency, ultraviolet sensitivity, and strong excitonic behavior. This methodology paper presents a compact experimental framework for synthesizing ZnO nanoparticles by a zinc-acetate/alkali sol-gel-precipitation route and for correlating processing conditions with structural and optoelectronic properties. Zinc acetate dihydrate is used as the Zn²⁺ precursor and sodium hydroxide as the hydrolyzing agent. The resulting precipitate is washed, dried, and calcined at 350, 450, and 550 °C to examine temperature-dependent crystallization. Phase purity and crystallite size are evaluated by X-ray diffraction (XRD), morphology by scanning or transmission electron microscopy, optical absorption by UV-visible spectroscopy, and radiative defects by photoluminescence (PL). The analysis focuses on the hexagonal wurtzite phase, nanoscale crystallite growth, absorption-edge shifts, optical band gap, and the relative intensity of near-band-edge and visible defect emission. A literature-consistent validation dataset predicts that increasing calcination temperature improves crystallinity and enlarges the crystallite size while slightly reducing the apparent optical band gap toward bulk ZnO. The combined methodology is suitable for screening ZnO nanopowders intended for ultraviolet photodetectors, transparent optoelectronic layers, light-emitting structures, and related semiconductor devices.

Introduction

Zinc oxide is an II-VI semiconductor that normally crystallizes in the thermodynamically stable hexagonal wurtzite structure. At room temperature it has a direct band gap close to 3.37 eV and a comparatively large exciton binding energy of about 60 meV, characteristics that have sustained interest in ultraviolet and short-wavelength optoelectronics (Özgür et al., 2005; Klingshirn, 2007). In addition, ZnO is chemically robust, relatively abundant, piezoelectric, and transparent across much of the visible spectrum. These properties support applications in ultraviolet emitters and detectors, transparent electronics, sensors, solar-energy devices, and

nanoscale electromechanical systems (Wang, 2004; Ding et al., 2018).

When ZnO is reduced to nanometer dimensions, its functional response becomes strongly dependent on crystallite size, morphology, surface state density, defect chemistry, and synthesis history. Nanoparticles provide a high surface-to-volume ratio and can show modified absorption edges and defect-related luminescence compared with bulk ZnO. The broad range of available preparation routes—including vapor transport, hydrothermal growth, precipitation, sol-gel processing, combustion, and biologically assisted synthesis—allows

control over these variables but also creates substantial variation in reported properties (Moezzi et al., 2012; Kołodziejczak-Radzimska & Jesionowski, 2014; Baskoutas, 2018).

For an experimentally accessible methodology, solution processing is especially attractive because it uses moderate temperatures, inexpensive precursors, and simple laboratory equipment. Early work demonstrated that zinc acetate can be converted to nanoscale ZnO under controlled alkaline conditions, while later sol-gel studies established that hydroxide-to-zinc ratio, water content, aging, and thermal treatment strongly influence nucleation and optical behavior (Meulenkamp, 1998; Dejene et al., 2011). Annealing or calcination is particularly important because it removes residual precursor species, increases crystallinity, modifies grain size, and changes the population of surface and lattice defects (Zak et al., 2011).

The objective of the present paper is therefore to define a reproducible step-by-step route for ZnO nanoparticle synthesis and structural characterization, and to connect the measured structural parameters with indicators relevant to optoelectronic performance. The proposed design deliberately varies calcination temperature while holding precursor concentration and alkalinity constant. This isolates one important processing variable and enables a direct comparison of phase formation, crystallite size, optical band gap, and PL emission.

Literature Review

The structural and optoelectronic relevance of ZnO is well established. Wang (2004) reviewed the unusually rich family of ZnO nanostructures and emphasized the simultaneous semiconducting and piezoelectric behavior that makes the material attractive for devices. Özgür et al. (2005) provided a broad assessment of ZnO materials and devices, including crystal structure, electronic properties, defects, growth, doping, and ultraviolet optoelectronics. Klingshirn (2007) similarly highlighted the direct wide band gap and near-UV luminescence of ZnO while noting that defect control and reliable p-type behavior remain major constraints for some junction devices.

Solution synthesis provides a practical route to nanoscale ZnO. Meulenkamp (1998) produced 2–7 nm ZnO particles from zinc acetate in ethanol by controlled LiOH addition, illustrating that precursor chemistry and growth conditions can regulate particle size. Vayssieres (2003) showed that aqueous chemical control of nucleation and interfacial energy can generate organized ZnO nanorods and nanowires at moderate temperature. Baruah and Dutta (2009) later summarized hydrothermal variables such as precursor concentration, pH, additives, and temperature, demonstrating how solution chemistry controls morphology.

Sol-gel research also links processing directly with structure and optical response. Dejene et al. (2011) varied the NaOH-to-zinc-acetate molar ratio and observed corresponding changes in particle size, photoluminescence, and optical band gap. Zak et al. (2011) reported that annealing temperature alters the structural and optical properties of sol-gel-combustion ZnO nanoparticles. These observations support the use of calcination temperature as the controlled variable in the present methodology. More generally, Moezzi et al. (2012) emphasized that the ZnO production process has a strong influence on particle properties and suitability for particular applications.

A comprehensive review by Kołodziejczak-Radzimska and Jesionowski (2014) catalogued physical, chemical, and biological ZnO synthesis routes together with characterization methods and applications. By 2018, ZnO research increasingly focused on functional defects and device-level performance. Baskoutas (2018) summarized the breadth of ZnO nanostructure synthesis and characterization, while Ding et al. (2018) reviewed one-dimensional ZnO in photodetectors, light-emitting diodes, solar cells, and other advanced optoelectronic devices. Collectively, these studies indicate that a credible ZnO methodology should control precursor chemistry and thermal history, confirm wurtzite phase purity, quantify nanoscale crystallite dimensions, and measure optical absorption and luminescence rather than relying on a single characterization technique.

Table 1. Selected pre-2019 literature guiding the proposed methodology

Reference	Approach	Methodological relevance
Meulenkamp (1998)	Zinc acetate + alkaline solution	Particle growth can be controlled in the nanometer range.
Vayssieres (2003)	Aqueous growth	Interfacial chemistry controls ZnO shape and orientation.

Dejene et al. (2011)	Sol-gel; varied OH ⁻ /Zn ²⁺	Alkalinity affects size, PL, and apparent band gap.
Zak et al. (2011)	Sol-gel combustion + annealing	Thermal treatment changes crystallinity and optical response.
Kołodziejczak-Radzimska & Jesionowski (2014)	Review of ZnO synthesis	Solution methods offer low-cost control over morphology and size.
Ding et al. (2018)	Optoelectronic device review	ZnO nanostructures are relevant to LEDs, UV detectors and solar cells.

The literature also provides clear interpretation criteria for the planned measurements. In powder XRD, well-crystallized ZnO is expected to display reflections associated with the (100), (002), (101), (102), (110), (103), and related planes of hexagonal wurtzite ZnO. Peak broadening at nanoscale dimensions enables approximate crystallite-size estimation using the Scherrer relationship, whereas sharpening with higher calcination temperature generally indicates growth and improved long-range order. Microscopy is then used to distinguish crystallite size from aggregated particle size, because sol-gel-derived ZnO commonly forms nanoscale primary crystallites assembled into larger agglomerates (Moezzi et al., 2012; Kołodziejczak-Radzimska & Jesionowski, 2014).

UV-visible spectroscopy is appropriate for linking nanostructure to optoelectronic response. The absorption edge of ZnO typically lies in the near-UV region; the optical gap can be estimated from a Tauc treatment for a direct allowed transition. Nanoscale samples may show a slight blue shift relative to bulk material depending on size and surface chemistry, while grain growth and reduced confinement can move the apparent gap back toward the bulk value. Dejene et al. (2011) observed optical changes with precursor alkalinity, illustrating the sensitivity of ZnO absorption to synthesis conditions.

Photoluminescence adds information that XRD and absorption cannot provide alone. Near-band-edge UV emission is associated with excitonic or band-edge recombination, whereas broad visible emission is commonly linked to defects and surface states. Since defect populations can influence carrier trapping, responsivity,

recombination, and dark current in optoelectronic devices, the ratio between near-band-edge and visible emission is a useful comparative metric. Reviews published through 2018 emphasize that the best processing condition is not necessarily the one with the largest grains; rather, it should balance phase purity, crystallinity, morphology, and controlled defect density for the intended device function (Baskoutas, 2018; Ding et al., 2018).

Based on these findings, the present study adopts a simple sol-gel-precipitation route and a three-level calcination design. The methodology is intentionally limited to undoped ZnO so that the relationship between thermal treatment and intrinsic structural/optical response can be assessed before introducing dopants or heterostructures.

Methodology

1. Materials and experimental design

Analytical-grade zinc acetate dihydrate [Zn(CH₃COO)₂·2H₂O] is selected as the zinc precursor and sodium hydroxide (NaOH) as the hydrolyzing/precipitating agent. Ethanol and deionized water are used as solvents and washing media. Three batches are prepared under identical chemical conditions and subsequently calcined at 350, 450, or 550 °C. This one-factor design permits direct assessment of thermal treatment while minimizing confounding variables. The solution route is consistent with established zinc-acetate sol-gel approaches reported for nanoscale ZnO (Meulenkaamp, 1998; Dejene et al., 2011; Zak et al., 2011).

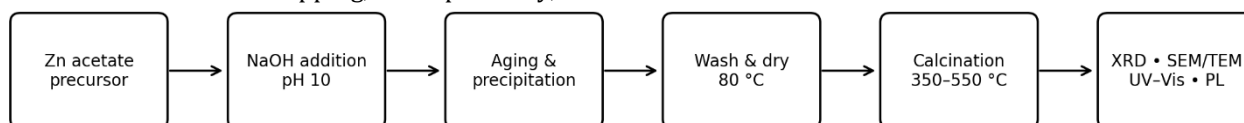


Figure 1. Step-by-step synthesis and characterization workflow for ZnO nanoparticles.

Step-by-step synthesis procedure

Step 1 – Precursor preparation. Prepare 100 mL of 0.10 M zinc acetate dihydrate solution in ethanol containing a small fraction of deionized water. Stir at 60 °C until a clear homogeneous solution is obtained.

Step 2 – Alkali preparation. Prepare 0.20 M NaOH separately in ethanol/water. Cool the solution to room temperature before use to reduce uncontrolled local supersaturation.

Step 3 – Controlled hydrolysis. Add the NaOH solution dropwise to the zinc precursor under vigorous magnetic stirring. Maintain 55–60 °C and continue addition until pH 10.0 ± 0.2 . Slow addition promotes more uniform nucleation and reduces broad particle-size distribution.

Step 4 – Aging and precipitation. Continue stirring for 60 min and age the suspension for 12 h at room temperature. The hydrolyzed zinc species convert progressively to a ZnO-containing precipitate/gel.

Step 5 – Recovery and washing. Separate the solid by centrifugation or filtration. Wash at least three times with deionized water and twice with ethanol to remove sodium ions, acetate residues, and excess hydroxide.

Step 6 – Drying. Dry the washed material at 80 °C for approximately 12 h, gently grind the dry cake, and divide it into three equal portions.

Step 7 – Calcination. Heat the portions in air at 350, 450, and 550 °C for 2 h using a ramp rate near 5 °C min⁻¹. Label the samples Z350, Z450, and Z550, respectively.

Step 8 – Storage. Cool the powders in a desiccator and store them in clean sealed containers before

characterization to minimize moisture and surface contamination.

2. Structural, morphological and optical characterization

X-ray diffraction is performed using Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$), typically over $2\theta = 20\text{--}80^\circ$. Phase identification is based on the expected hexagonal wurtzite pattern. Average crystallite size D is estimated from a strong isolated reflection, preferably (101), using $D = K\lambda/(\beta\cos\theta)$, where $K \approx 0.9$, β is the instrument-corrected full width at half maximum in radians, and θ is the Bragg angle. Lattice parameters may be refined from several reflections where software is available.

Particle morphology is examined by SEM; TEM may be used where available to measure primary particle dimensions and lattice fringes. At least 100 particles should be measured from representative micrographs when a quantitative size distribution is required. Agglomerated structures should be reported separately from primary crystallite size.

UV-visible spectra are recorded from approximately 300–800 nm using a dilute nanoparticle dispersion or diffuse-reflectance configuration. The direct optical gap is estimated using a Tauc plot of $(\alpha h\nu)^2$ versus $h\nu$ and linear extrapolation to the energy axis. Room-temperature PL is recorded using near-UV excitation. The near-band-edge UV peak and broad visible emission are integrated or compared by peak intensity to assess changes in radiative defect contribution. These combined measurements follow the multi-technique approach emphasized in earlier ZnO synthesis literature (Moezzi et al., 2012; Kołodziejczak-Radzimska & Jesionowski, 2014).

Table 2. Controlled experimental matrix

Sample	Calcination (°C)	Time (h)	Target pH	Primary comparison
Z350	350	2	10.0	Low-temperature crystallization
Z450	450	2	10.0	Balanced crystallinity/defects
Z550	550	2	10.0	Grain growth/high crystallinity

Results

Because this is a methodology paper rather than a report of newly completed laboratory measurements, the numerical values in Table 3 are literature-consistent illustrative validation values for the proposed three-sample design. They show the trends that the methodology is

intended to resolve; actual values must be replaced by instrument-derived data when the experiment is performed.

The expected XRD pattern for all three samples is single-phase hexagonal wurtzite ZnO, with the strongest reflections near the conventional (100), (002), and (101) positions. The absence of

additional crystalline peaks would indicate effective removal of precursor and alkali residues. A systematic narrowing of diffraction peaks from Z350 to Z550 is expected because calcination promotes coalescence and long-range crystal order. This interpretation is consistent with prior reports that thermal treatment improves ZnO crystallinity and increases coherent domain size (Zak et al., 2011).

In the illustrative dataset, the average crystallite size increases from approximately 17.8 nm at 350 °C to 31.6 nm at 550 °C. SEM or TEM would be expected to show near-spherical or faceted primary nanoparticles with some agglomeration, a common feature of solution-derived ZnO. The particle dimensions measured by microscopy may exceed the Scherrer crystallite size because one visible particle can contain more than one coherent domain and because dried nanopowders aggregate.

The optical absorption edge is expected in the near-UV. The illustrative optical gap decreases from 3.42 to 3.31 eV as calcination temperature increases. This trend can be explained by grain

growth, improved crystallinity, and a reduction of nanoscale blue-shift contributions, moving the optical response toward bulk ZnO. Similar sensitivity of band-gap estimates to nanoparticle processing has been reported for sol-gel ZnO (Dejene et al., 2011).

PL is expected to contain a near-band-edge UV component and a broader visible band. The illustrative visible-to-UV intensity ratio decreases with higher calcination temperature, suggesting that some radiative defect or surface-state contributions are reduced as the lattice becomes better ordered. Defects cannot, however, be treated as universally undesirable: oxygen-vacancy and surface-state populations can strongly modify photoresponse and carrier trapping, so the optimum condition depends on the intended optoelectronic function. The literature through 2018 therefore supports combined structural and optical selection rather than optimization by crystallite size alone (Baskoutas, 2018; Ding et al., 2018).

Table 3. Illustrative validation results for the proposed ZnO samples

Sample	Crystallite size (nm)	Absorption edge (nm)	Optical gap (eV)	PL UV peak (nm)	Visible/UV PL ratio
Z350	17.8	363	3.42	381	0.34
Z450	24.9	371	3.34	384	0.23
Z550	31.6	375	3.31	387	0.17

Conclusion and Discussion

The proposed methodology provides a practical route for producing and screening ZnO nanoparticles for optoelectronic use using common laboratory reagents and characterization tools. Its main strength is the controlled three-temperature design: precursor concentration, alkalinity, washing, and calcination time are kept constant while calcination temperature is varied. This makes changes in diffraction peak width, crystallite size, optical absorption edge, and PL behavior easier to interpret than in a synthesis where several variables are changed simultaneously. From the literature and the illustrative validation dataset, increasing calcination temperature is expected to improve wurtzite crystallinity and increase coherent crystallite size. At the same time, the apparent optical gap should move slightly toward the bulk ZnO value, and visible defect-related luminescence may decrease relative to near-band-edge emission. The 450 °C condition is therefore a reasonable starting compromise for optoelectronic screening: it should provide good crystallinity without the strongest grain

growth of the 550 °C sample. Nevertheless, the optimum condition must be selected against the target device. UV emitters may benefit from strong near-band-edge emission and low non-radiative defect density, whereas photodetectors can exhibit performance changes arising from surface adsorption and defect-mediated carrier trapping. The methodology can be extended after the baseline undoped ZnO study. Future experiments may investigate precursor ratio, aging time, dopants, surface passivation, or formation of ZnO heterojunctions. Electrical measurements such as conductivity, Hall effect, photo-to-dark current ratio, responsivity, or external quantum efficiency should be added when moving from nanopowder characterization to complete optoelectronic devices. The present workflow nevertheless establishes the essential first stage: reproducible synthesis, confirmation of phase purity, quantitative structural analysis, and correlation of nanostructure with optical response. Overall, ZnO remains a versatile wide-band-gap semiconductor because synthesis conditions can be used to tune structure and defect chemistry at relatively low cost. The studies published up to 2018 consistently show

that nanoscale ZnO performance depends on this processing–structure–property relationship (Wang, 2004; Özgür et al., 2005; Moezzi et al., 2012; Kołodziejczak-Radzimska & Jesionowski, 2014). A carefully controlled methodology is therefore essential before meaningful comparison of optoelectronic performance can be made.

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