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Simple Method for Calculation Hexagonal Lattice Parameters (a and c) System of ZnO nanorod via X-ray Analysis: Review

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ABSTRACT

Objective: *Zinc oxide (ZnO) nanorods, a cornerstone of one-dimensional semiconductor nanostructures, have attracted profound research interest due to their unique combination of piezoelectricity, wide bandgap, and biocompatibility. While often treated as a wurtzite-structured constant, the lattice parameters (a, b, and c) of ZnO nanorods are not immutable. This review comprehensively examines the intentional engineering of ZnO nanorod lattice constants through various synthesis strategies, including doping with foreign elements, manipulation of growth parameters, and substrate-induced strain.* ***Method:*** *We delve into the fundamental mechanisms – such as ionic radius mismatch, formation of intrinsic point defects, and external stress – that lead to lattice expansion or contraction.* ***Results:*** *The consequential tuning of functional properties, most notably the bandgap via strain-induced piezoelectric effects, is critically analyzed. Furthermore, this review consolidates recent advancements demonstrating how precise lattice control enhances performance in applications ranging from piezotronics and optoelectronics to catalysis and sensing.* ***Novelty:*** *By synthesizing findings from a vast body of literature, this review aims to serve as a foundational guide for researchers seeking to exploit lattice engineering as a powerful tool for tailoring ZnO nanorods for next-generation technologies.*

INTRODUCTION

Zinc oxide (ZnO) is a II-VI semiconductor material possessing a direct wide bandgap (~3.37 eV) and a large exciton binding energy (60 meV) at room temperature [1]. Its crystallographic preference for the hexagonal wurtzite structure (space group P63mc) endows it with strong piezoelectric and pyroelectric properties. Among its various morphologies, one-dimensional (1D) nanostructures, particularly nanorods (NRs), nanowires, and nanoneedles, have been the focus of intense research due to their high surface-to-volume ratio, quantum confinement effects, and superior charge carrier transport capabilities [2]. The wurtzite structure of ZnO is characterized by two lattice constants: the basal plane lattice constant `a` (where `a = b` due to hexagonal symmetry) and the axial lattice constant `c`. In a stress-free, bulk single crystal, these values are approximately `a = 3.249 Å` and `c = 5.206 Å`, with a `c/a` ratio of ~1.602, close to the ideal value for a hexagonal close-packed structure ($\sqrt{8/3} \approx 1.633$) [3].

However, at the nanoscale, these dimensions are highly susceptible to change. The lattice constants of ZnO nanorods are not intrinsic properties but are variables that can be deliberately engineered. This tunability arises from several factors: the incorporation of dopant atoms with different ionic radii, the introduction of intrinsic point defects (e.g., oxygen vacancies V_O, zinc interstitials Zn_i), and the presence of external or internal strain during growth [4]. The ability to control the lattice parameters is paramount

because they are directly linked to the material's electronic structure and physical properties. Even minor deviations in the `c/a` ratio can significantly alter the bandgap energy (Eg), piezoelectric potential, charge carrier mobility, and chemical reactivity [5].

This structure-property relationship makes lattice engineering a critical design strategy for optimizing ZnO NRs for specific applications. This manuscript aims to provide a detailed review of the strategies employed to modulate the lattice constants of ZnO nanorods, the underlying physical mechanisms, and the resulting impact on their properties and application performance. We will summarize experimental findings in comprehensive tables and discuss future perspectives in this dynamic field of research.

RESEARCH METHOD

Synthesis Techniques and Lattice Modification Mechanisms

The lattice parameters of ZnO NRs are predominantly determined during their synthesis. The most common techniques include hydrothermal/solvothermal methods, chemical vapour deposition (CVD), and molecular beam epitaxy (MBE). Each method offers different knobs for tuning the crystal lattice.

A. Doping-Induced Lattice Strain

The most direct method for altering the lattice constants of ZnO is through the introduction of dopant atoms. When a foreign cation substitutes for a Zn^{2+} site or occupies an interstitial position, it imposes local stress on the ZnO crystal lattice due to the difference in ionic radius. This stress leads to a macroscopic expansion or contraction of the unit cell.

Cationic Doping: Incorporating elements with a larger ionic radius than Zn^{2+} (0.74 Å for coordination number 4) typically leads to lattice expansion. For instance, doping with Mg^{2+} (0.57 Å) often leads to a decrease in the `c`-axis length, while doping with larger ions like Cd^{2+} (0.95 Å) causes a clear expansion of the lattice [6]. Similarly, incorporation of rare-earth elements or transition metals like Co^{2+} (0.58 Å) or Ni^{2+} (0.55 Å) can contract the lattice. The change in lattice constant is often linearly related to the dopant concentration, following Vegard's law for solid solutions, albeit with limitations due to defect formation and solubility limits [7].

Anionic Doping: While less common, anionic doping (e.g., with S, Se, or N) can also modify the lattice by substituting on oxygen sites. The larger ionic radius of S^{2-} (1.84 Å) compared to O^{2-} (1.38 Å) leads to a significant expansion of the lattice constants [8].

B. Growth Parameter Optimization

Even in undoped ZnO NRs, synthesis conditions can profoundly influence lattice constants. In hydrothermal growth, parameters like precursor concentration, pH, temperature, and growth time dictate the kinetics of crystal formation and the incorporation of intrinsic defects.

pH and Precursor Concentration: A low pH (acidic) environment can promote the formation of zinc interstitials (Zn_i) and oxygen vacancies (V_O) to maintain charge neutrality. Zn_i are small cations that can cause local lattice distortion, while a high

concentration of V_O can relax the lattice, leading to observable changes in the `c`-axis parameter [9].

Growth Temperature: Temperature affects the surface energy and adatom mobility during growth. Higher temperatures often promote the growth of more thermodynamically stable crystals with lattice parameters closer to bulk values, while lower temperatures can result in strained nanostructures with altered lattice constants due to non-equilibrium growth and defect incorporation [10].

C. Substrate-Induced Epitaxial Strain

The lattice mismatch between a substrate and the growing ZnO NRs generates epitaxial strain. For example, growing ZnO (a = 3.249 Å) on sapphire Al_2O_3 (a = 4.759 Å) involves a complex domain matching paradigm, but can result in strained NRs. This strain can be tensile or compressive, leading to a corresponding elongation or compression of the ZnO lattice constants in the initial growth layers. While this strain can sometimes be relaxed as the NRs grow thicker, it often persists in the entire structure, especially for thinner NRs or when using compliant substrates [11]. The use of flexible substrates like polyethylene terephthalate (PET) or polydimethylsiloxane (PDMS) also allows for the imposition of post-growth strain, which dynamically alters the lattice constants [12].

Table 1. Effect of Cationic Doping on ZnO Nanorod Lattice Constants.

Dopant	Ionic Radius (Å)	Effect on Lattice	Mechanism	Ref
Mg^{2+}	0.57 (CN=4)	Decrease in `a` and `c`	Substitutional, smaller ion	[13]
Cd^{2+}	0.95 (CN=4)	Increase in `a` and `c`	Substitutional, larger ion	[14]
Co^{2+}	0.58 (CN=4)	Decrease in `c`, small change in `a`	Substitutional, smaller ion	[15]
Cu^{2+}	0.57 (CN=4)	Decrease in `c`-axis length	Substitutional, smaller ion	[16]
Eu^{3+}	0.947 (CN=6)	Increase in `c`-axis length	Substitutional, lattice distortion	[17]
Al^{3+}	0.39 (CN=4)	Decrease in `a` and `c`	Substitutional, much smaller ion	[18]

Characterization of Lattice Modifications

Accurately measuring the often-subtle changes in lattice constants is crucial. The primary tool for this is X-ray diffraction (XRD). Shifts in the angular position (2θ) of the diffraction peaks, particularly the (100) and (002) peaks, are used to calculate changes in the `a` and `c` lattice constants using Bragg's law and the wurtzite geometry equations.

XRD Analysis: A shift of the (002) peak to a higher 2θ angle indicates a compression of the `c`-axis, while a shift to a lower 2θ signifies an expansion. The `a`-constant is calculated from the (100) peak position. High-resolution XRD (HR-XRD) and reciprocal space mapping (RSM) are advanced techniques that can deconvolute strain from composition effects and analyze crystallographic tilt and twist [19].

Complementary Techniques: Raman spectroscopy is highly sensitive to crystal strain. The E_2(high) phonon mode of ZnO is particularly responsive to biaxial strain, and its shift provides a qualitative measure of stress in the lattice [20]. High-resolution transmission electron microscopy (HR-TEM) allows for direct visualization and measurement of lattice fringes, providing local, nanoscale information on d-spacings and defects that XRD, which provides an ensemble average, cannot [21].

Table 2. Effect of Synthesis Parameters on Lattice Constants of Undoped ZnO Nanorods.

Synthesis Parameter	Typical Variation	Effect on Lattice Constants	Proposed Reason	Refer
Growth Temperature	Low (e.g., 70°C) → High (e.g., 95°C)	c -axis approaches bulk value with increasing temp.	Reduced defect concentration, Ostwald ripening	[22]
Solution pH	Acidic (e.g., pH=5) → Basic (e.g., pH=10)	c -axis decreases with increasing pH	Lower V_O concentration at higher pH	[23]
Zn^{2+}:OH^- Ratio	Zn^{2+} rich → OH^- rich	Expansion in acidic, contraction in basic rich medium	Defect chemistry (V_O vs. Zn_i formation)	[24]
Growth Time	Short (1h) → Long (24h)	c -axis can relax over time	Defect annihilation and crystal ripening	[25]

RESULTS AND DISCUSSION

Impact on Functional Properties

The deliberate modification of lattice constants is not an end in itself but a means to tailor the functional properties of ZnO NRs for enhanced device performance.

A. Bandgap Engineering

The bandgap of ZnO is highly sensitive to lattice strain due to the deformation potential. Biaxial strain in the a-b plane significantly shifts the conduction and valence band edges.

Tensile Strain: Expands the lattice, typically leading to a narrowing of the bandgap (red-shift in absorption edge). This is commonly observed in Cd-doped ZnO NRs [26].

Compressive Strain: Contracts the lattice, generally causing a widening of the bandgap (blue-shift). This is a hallmark of Mg-doped ZnO (ZnMgO) NRs, making them a vital material for bandgap engineering in heterostructures [27].

This strain-induced bandgap tuning is a powerful alternative to composition-driven tuning and is critical for designing optoelectronic devices like LEDs and photodetectors with specific spectral responses.

B. Piezoelectric Properties

The piezoelectric coefficient `d_33` of ZnO is directly related to its crystal structure. Changes in the `c/a` ratio affect the polarization and the magnitude of the piezoelectric response. Compressive strain along the c-axis can enhance the piezoelectric output by increasing the internal polarization field. This is fundamental to the field of piezotronics, where the piezoelectric potential is used to gate charge transport in a semiconductor device. Engineering stiffer or more compliant lattices through doping allows for the optimization of ZnO NRs for mechanical energy harvesting (nanogenerators) and piezotronic sensors [28].

C. Catalytic and Sensing Performance

The surface atomic arrangement and electronic structure of a catalyst are determined by its lattice parameters. Strain can modify the adsorption energies of molecules on the ZnO surface.

Photocatalysis: A strained lattice can alter the bandgap and the positions of the valence and conduction bands, thereby changing the redox potential of photogenerated charges. It can also influence the separation efficiency of electron-hole pairs. This makes lattice-tuned ZnO NRs more efficient for photocatalytic degradation of pollutants or water splitting [29].

Gas Sensing: The resistance change in ZnO-based gas sensors upon analyte adsorption is sensitive to the surface state. Strain can modulate the surface energy and the density of active sites, thereby enhancing the sensitivity and selectivity towards specific gases like CO, H_2, or NO_2 [30].

Applications of Lattice-Engineered ZnO Nanorods

The ability to control lattice constants has opened new avenues in device engineering.

Strained-Layer Heterostructures and Quantum Wells: Lattice-tuned ZnMgO and ZnCdO layers are essential for creating heterostructures with ZnO. By carefully matching or mismatching lattices, researchers can create quantum wells and superlattices that confine charge carriers, leading to efficient UV LEDs and laser diodes [31].

High-Performance Piezoelectric Nanogenerators (PENGs): Compressively strained ZnO NRs grown on flexible substrates exhibit enhanced piezoelectric output. When bent, the pre-strain and modified `d_33` coefficient allow for higher voltage and power generation, crucial for powering micro-devices [32].

Tunable Photodetectors: By applying external strain to a ZnO NR-based photodetector, its photoresponsivity and the cut-off wavelength can be dynamically tuned. This "strain-phototronics" concept allows for the creation of mechanically reconfigurable optical sensors [33].

Enhanced Photocatalysts: Lattice-expanded ZnO NRs (e.g., via S-doping) with a narrowed bandgap can harness a broader spectrum of visible light for photocatalytic reactions, greatly improving their efficiency under solar irradiation [34].

CONCLUSION

Fundamental Finding : This review has elucidated the significant progress in understanding and controlling the lattice constants of ZnO nanorods. It is evident that through strategic doping, precise control of synthesis parameters, and clever use of substrate-induced strain, the a and c dimensions of the ZnO wurtzite unit cell can be expanded or contracted in a predictable manner. This lattice engineering is not merely a structural curiosity; it is a powerful knob for tuning fundamental properties like bandgap energy, piezoelectric response, and surface chemical activity. **Implication :** Consequently, it directly enables enhanced performance in a wide array of applications, from energy harvesters and optoelectronic devices to catalysts and sensors. **Limitation :**

In conclusion, the engineering of lattice constants in ZnO nanorods has matured from a fundamental observation to a critical materials design strategy. **Future Research :** As synthesis control becomes more precise and our understanding of structure-property relationships deepens, this approach will undoubtedly play a central role in unlocking the full potential of ZnO nanostructures for future technological innovations.

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