

Effect of growth temperature variation on the morphology and performance of dye-sensitized solar cells based on magnesium-doped zinc oxide nanorods

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ABSTRACT

This study investigates the effect of growth temperature variation on the morphology, optical properties, and performance of dye-sensitized solar cells (DSSC) based on Mg-doped ZnO nanorods. The nanorods were synthesized using a seed-mediated hydrothermal method on FTO substrates with 4% Mg concentration and growth temperatures ranging from 70°C and 90°C. Material characterization was conducted using UV-Vis spectroscopy, XRD, FESEM, and EDX. The results indicate that growth temperature significantly influences the structure and distribution of ZnO nanorods, affecting dye absorption and electron transport. Optimal temperature conditions produce more uniform morphology and enhance DSSC performance. Therefore, growth temperature is a key parameter in optimizing ZnO:Mg materials for solar cell applications.

Keywords: DSSC; efficiency; nanorods; temperature; ZnO:Mg

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INTRODUCTION

The energy crisis is intensifying due to the rising demand for electricity-derived from fossil fuels-to power urban buildings [1]. Widespread fossil fuel usage results in significant carbon emissions, which in turn drive global warming and energy-related issues; consequently, developing renewable energy sources is essential to mitigate environmental impacts [2].

In efforts to address the adverse effects of fossil fuel consumption, innovation in solar cell technology has become a focal point within the renewable energy sector. Unlike coal-a primary driver of carbon emissions and global warming-this technology offers a clean energy alternative that supports sustainability [3]. The dye-sensitized solar cell (DSSC) represents a third-generation solar cell innovation that operates by absorbing light. DSSCs were first introduced by Grätzel and O'Regan in 1991. This technology offers numerous advantages-such as low production costs, simple manufacturing processes, environmental friendliness, and minimal pollution-making it a promising energy option [4]. The main components of a DSSC include a

photoanode, a dye, an electrolyte, and a counter electrode. The photoanode, typically composed of metal oxides (such as TiO_2 and ZnO), plays a crucial role in the electron transfer process while also hosting the dye molecules [4].

Zinc oxide (ZnO) is a promising semiconductor for DSSC applications due to its ease of synthesis, low cost, non-toxicity, and favorable optical and electrical properties. It possesses a wide bandgap of approximately 3.3 eV, meaning it primarily absorbs light within the UV spectrum [5]. ZnO offers a high capacity for increasing surface area, which enhances light absorption and, consequently, improves overall efficiency [6]. ZnO nanorods suffer from certain drawbacks, such as rapid electron recombination with the electrolyte and low surface capacity for dye adsorption, which reduce DSSC performance efficiency [7].

Magnesium (Mg) doping modifies the material's electronic structure by widening the energy bandgap and enhancing electrical conductivity, thereby boosting the efficiency of ZnO -based optoelectronic devices and solar cells [8]. Incorporating magnesium into ZnO improves light absorption efficiency as well as optical

and electrical characteristics [9]. Mg is a suitable dopant for ZnO because its ionic radius (0.57 Å) is very close to that of Zn^{2+} (0.60 Å), allowing it to substitute for Zn in the crystal lattice without causing significant distortion [10].

The seed-mediated hydrothermal method combines seed-mediated growth and hydrothermal techniques, making it an effective approach for nanoparticle synthesis. This method is easy to implement, requires no expensive equipment, and operates at low temperatures and pressures. It is ideal for fabricating high-quality ZnO nanorod structures directly onto substrates, which serve as working electrodes in DSSCs [11]. Temperature variations are employed during the synthesis of Mg-doped ZnO because temperature plays a crucial role in controlling crystal growth, morphology, and the quality of the resulting nanorod structures [12].

ZnO is a promising alternative to TiO_2 for DSSCs due to its higher electron mobility and the potential for increased power conversion efficiency upon Mg doping [13]. This study investigates the effect of growth temperatures (70°C and 90°C) on the optical properties, crystal structure, morphology, and efficiency of Mg-doped ZnO nanorod-based DSSCs fabricated via the seed-mediated hydrothermal method.

RESEARCH METHODS

Synthesis of ZnO:Mg Nanorods via Seed-Mediated Hydrothermal Method

The synthesis of ZnO:Mg nanorods was carried out in two main stages: seeding and growth. FTO substrates (2.0 cm × 1.2 cm) were first cleaned with Decon detergent, rinsed with tap water and deionized (DI) water, and then sequentially sonicated in DI water, ethanol, and DI water in an ultrasonic bath at 60°C for 15 minutes each; finally, they were dried in an oven at 90°C for 15 minutes. In the seeding stage, a seed solution was prepared by dissolving zinc acetate dihydrate (ZAD) in 10 ml of ethanol. A 200 µl aliquot of the solution was dropped onto an FTO substrate that had been preheated on a hot plate at 100°C for 15 minutes. Subsequently,

the substrate was annealed in an oven at 250°C for 1 hour to strengthen the ZnO seed layer.

In the growth stage, 0.595 g of zinc nitrate hexahydrate (ZNH) was dissolved in 10 ml of DI water, and 0.14 g of hexamethylenetetramine (HMT) was dissolved in another 10 ml of DI water. The seeded FTO substrate was placed into a synthesis vial at an inclination of approximately 45°. A 4 mol% Mg doping solution was prepared by dissolving 0.3 g of Mg in 1 ml acetone and adding it to the growth solution. The synthesis vial was then heated in an oven for 8 hours at varying temperatures: 70°C and 90°C.

DSSC Fabrication

The counter electrode was prepared by coating FTO with a plastisol solution applied via uniform dropping, heating it on a hot plate at 100°C for 10 minutes (repeated three times), then immersing the substrate in an AgNO_3 solution (dissolved in deionized water) and heating it in an oven at 90°C for 8 hours. The natural dye was prepared from 25 grams of crushed dragon fruit peel; 80 ml of ethanol and 20 ml of distilled water were added, the mixture was sonicated for 30 minutes, and then left to soak for 3 hours. The electrolyte was prepared by dissolving 0.8 g of KI in 10 ml of acetonitrile and adding 0.127 g of iodine; this mixture was then combined with PEG 400 gel and chloroform and stirred at 80°C for 60 minutes. The commercial electrolyte iodolyte AN-50 was also used for performance testing. DSSC fabrication involved assembling the components into a sandwich structure. The working electrode (FTO + ZnO : Mg + dye) was placed over the counter electrode (FTO + plastisol + AgNO_3). The active testing area was defined using Parafilm to create a circular area of 0.25 cm². The two electrodes were clamped together, followed by the injection of the iodolyte AN-50 electrolyte.

Characterization

Optical properties were analyzed using UV-Vis spectroscopy over a wavelength range of 200 – 800 nm. The band gap energy was deter-

mined using the Tauc plot method based on the equation $(\alpha h\nu)^2 = A (h\nu - E_g)$. The crystal structure of the samples was identified using X-ray diffraction (XRD) over a 2θ angle range of $20^\circ - 60^\circ$. Crystallite size was calculated using the Scherrer equation: $D = K\lambda / (b\cos\theta)$. The surface morphology of the samples was analyzed using field emission scanning electron microscopy (FESEM) at magnifications up to $10,000\times$. The elemental composition of the samples was identified using energy dispersive X-ray (EDX).

RESULTS AND DISCUSSION

UV-Vis Results

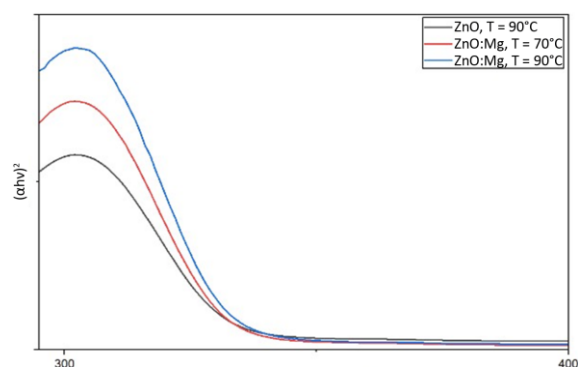


Figure 1. Absorption spectra of Mg-doped ZnO samples grown at various temperatures.

Figure 1 shows the absorbance spectra as a function of wavelength for Mg-doped ZnO samples grown at various temperatures. The results indicate that the highest absorption intensity occurs in the ultraviolet region, within the 300 – 400 nm wavelength range [14]. The maximum absorbance values for the ZnO, ZnO:Mg (70°C), and ZnO:Mg (90°C) samples are 1.16, 1.48, and 1.37 a.u., respectively. The highest absorption value was observed for the ZnO:Mg sample grown at 90°C (1.37 a.u.), while the lowest value was found in the undoped ZnO sample (1.16 a.u.).

Sample absorption increased significantly as the growth temperature rose from 70°C to 90°C. This increase in absorption is associated with the emergence of additional energy levels within the ZnO structure, whereas a decrease in absorption is influenced by reduced crystal quality, leading to increased photon scattering

[15]. The energy gap was determined by extrapolating the straight-line portion of the Tauc plot until it intersected the x-axis. Undoped ZnO exhibited an energy gap of 3.35 eV, which falls within the typical energy gap range for ZnO materials [16]. Mg doping of ZnO at growth temperatures of 70°C and 90°C resulted in lower energy gap values compared to pure ZnO. This phenomenon is attributed to the formation of additional energy levels between the valence and conduction bands, resulting from the interaction of Mg electrons with the electronic structure of ZnO [17]. The energy gap values for all samples are presented in Table 1.

Table 1. Band gap of Mg-doped ZnO nanorods grown at various temperatures.

Sample	Energy gap (eV)
ZnO	3.35
ZnO:Mg 70°C	3.16
ZnO:Mg 90°C	3.14

X-Ray Diffraction Pattern Analysis

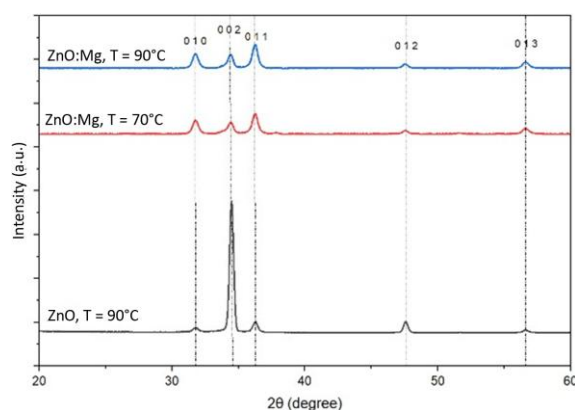


Figure 2. XRD patterns of Mg-doped ZnO samples grown at various temperatures.

Figure 2 shows the diffraction patterns of ZnO and Mg-doped ZnO samples grown at various temperatures. The results reveal five diffraction peaks at 2θ angles of 31.74° , 34.46° , 36.29° , 47.57° , and 56.69° , corresponding to the (010), (002), (011), (012), and (110) crystal planes. Analysis using High Score software confirms that the samples possess a hexagonal wurtzite structure, consistent with JCPDS database file number 36-1451 [18]. The highest peak occurs at $2\theta = 34.46^\circ$ (crystal plane

(002)), indicating that the ZnO with a hexagonal wurtzite crystal structure has lattice parameters of $a = 3.25 \text{ \AA}$ and $c = 5.21 \text{ \AA}$ (see Figure 3).

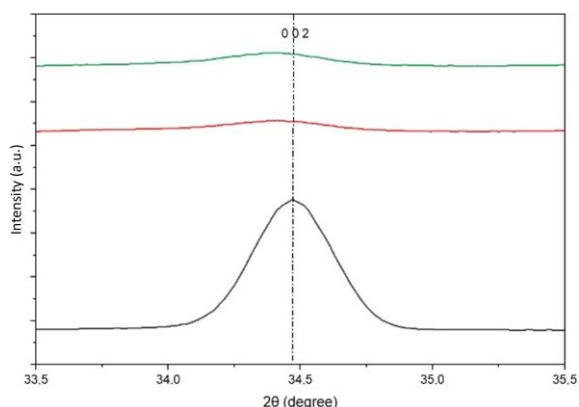


Figure 3. Diffraction peak shift for the (002) plane.

All samples—both ZnO and Mg-doped ZnO—exhibit diffraction peaks characteristic of the hexagonal wurtzite crystal structure, indicating that the Mg doping process and variations in growth temperature did not alter the primary crystalline phase of the ZnO. At the lower temperature (70°C), peak intensities tend to be lower and the peaks broader, indicating suboptimal crystallinity and relatively small crystallite sizes. In the ZnO:Mg samples, a shift in the diffraction peak toward higher 2θ angles is observed compared to pure ZnO; this indicates a contraction of the lattice parameters resulting from the substitution of Zn^{2+} ions with Mg^{2+} ions—which have a smaller ionic radius—within the ZnO wurtzite structure [19].

Table 2. Presents the FWHM values and crystal sizes of Mg-doped ZnO nanorods grown at various temperatures.

Sample	FWHM	Crystal size (nm)
ZnO	0.29	35.34
ZnO:Mg 70°C	0.28	30.77
ZnO:Mg 90°C	0.23	40.06

The FWHM values and crystallite sizes for all samples are presented in Table 2. The ZnO:Mg sample prepared at 90°C yielded an FWHM value of 0.23 and the largest crystallite size (40.06 nm), whereas the ZnO:Mg sample prepared at 70°C exhibited the smallest crystallite size (30.77 nm).

FESEM Characterization

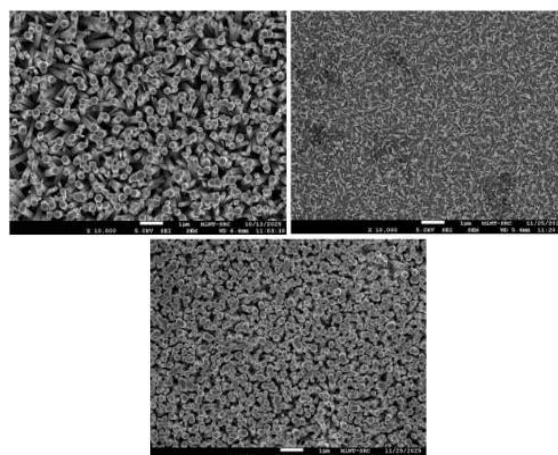


Figure 4. FESEM images of pure ZnO and ZnO:Mg nanorods grown at temperatures of 70°C and 90°C (10,000× magnification).

Figure 4 displays FESEM images showing the morphology of ZnO and ZnO:Mg samples grown at 70°C and 90°C at 10,000× magnification. The images reveal hexagonal ZnO nanorods, with diameters varying across samples with synthesis temperature. Pure ZnO (90°C) exhibits hexagonal nanorods with diameters of approximately 74 – 104 nm. [20]. At 70°C, more distinct grain growth is observed, characterized by better-defined particles and reduced agglomeration. At 90°C, the morphology becomes more uniform, with homogeneous size distribution and low agglomeration, indicating balanced nucleation and crystal growth [21].

Increasing synthesis temperature produces larger particles through enhanced atomic diffusion. At excessively high temperatures, particles may coalesce and agglomerate [22]. FESEM observations indicate the best morphology at 90°C, with relatively homogeneous particle sizes and minimal agglomeration.

CONCLUSION

ZnO:Mg nanorods were successfully synthesized on FTO using a seed-mediated hydrothermal method. At 90°C, UV-Vis measured an absorbance of 1.37 a.u.; XRD confirmed a hexagonal wurtzite structure with a maximum crystallite size of 40.06 nm; and FESEM showed

the most uniform morphology. EDX confirmed Mg presence in the samples.

AUTHOR CONTRIBUTIONS

Iwantono: Conceptualization, methodology, supervision, review and editing. Rihla Datul Aisy: Investigation, data curation, analysis, visualization, original draft. Marlia Morsin: Validation, review and editing. Friska Ziliwu: Investigation, analysis, review and editing. All authors approved the manuscript.

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DECLARATION OF AI USE

The authors declare that no AI tools were used to prepare this manuscript.

CONFLICT OF INTEREST

The authors declare no conflicts of interest.

DATA AVAILABILITY STATEMENT

All supporting data are included in this article. No additional datasets are available.

ETHICAL APPROVAL

Ethical approval was unnecessary, as no humans or animals were involved.

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