Effects of Sulfur Doping and Temperature on the Energy Bandgap of ZnO Nanoparticles and Their Antibacterial Activities

Kenassa Wakgari Aga, Mulugeta Tesema Efa, and Tamene Tadesse Beyene*

ABSTRACT: Metal oxide nanoparticles (MO-NPs) are presently an area of intense scientific research, attributable to their wide variety of potential applications in biomedical, optical, and electronic fields. MO-NPs such as zinc oxide nanoparticles (ZnO-NPs) and others have a very high surface-area-to-volume ratio and are excellent catalysts. MO-NPs could also cause unexpected effects in living cells because their sizes are similar to important biological molecules, or parts of them, or because they could pass through barriers that block the passage of larger particles. However, undoped MO-NPs like ZnO-NPs are chemically pure, have a higher optical bandgap energy, exhibit electron–hole recombination, lack visible light absorption, and have poor antibacterial activities. To overcome these drawbacks and further outspread the use of ZnO-NPs in nanomedicine, doping seems to represent a promising solution. In this paper, the effects of temperature and sulfur doping concentration on the bandgap energy of ZnO nanoparticles are investigated. Characterizations of the synthesized ZnO-NPs using zinc acetate dihydrate as a precursor by a sol–gel method were done by using X-ray diffraction, ultraviolet–visible spectroscopy, and Fourier transform infrared spectroscopy.

A comparative study was carried out to investigate the antibacterial activity of ZnO nanoparticles prepared at different temperatures and different concentrations of sulfur-doped ZnO nanoparticles against Staphylococcus aureus bacteria. Experimental results showed that the bandgap energy decreased from 3.34 to 3.27 eV and from 3.06 to 2.98 eV with increasing temperature and doping concentration. The antibacterial activity of doped ZnO nanoparticles was also tested and was found to be much better than that of bare ZnO nanoparticles.

1. INTRODUCTION

Nanoparticle (NP) investigation is presently a field of intense scientific research, attributable to a wide diversity of latent applications, such as biomedical, optical, and electronic fields. More importantly, semiconducting metal oxide nanoparticles (MO-NPs) have been treated with great consideration for their benefits such as fast and profound detection, portability, biomedical applications in drug delivery systems, high microbial action, and relatively low cost compared to other conventional procedures. However, their high-energy bandgap is hindering their potential applications. The bandgap energy of a semiconductor designates the energy required to excite an electron from the valence band (VB) to the conduction band (CB). The optical bandgap energy \( E_g \) and absorption coefficient \( \alpha \) are linked by the equation (Tauc method) \[ \alpha h \nu = A (h \nu - E_g) \] Here, \( h \) is the acting photon energy. The variation of \( \alpha h \nu \) with \( h \nu \) is plotted for a metal oxide nanoparticle annealed at different temperatures and different doping concentrations. In semiconductors, electrons could make a jump from the VB to the CB but not with the same ease as they do in conductors, since the gap between the VB and CB is larger in the case of semiconductors. Spectrophotometric techniques are used to find the energy bandgap in semiconductors. The energy bandgap was assessed from the intercept of the linear portion of the individual curve for various annealing temperatures through the \( h \nu \) on the x-axis.

MO-NPs are special classes of nanomaterials that have harvested huge interest in the fields of systematic research and in many supplementary practical disciplines because of their chemical and physical properties and numerous actual applications. Engineered MO-NPs are among the widest used and manufactured nanomaterials. Among MO-NPs, ZnO-NPs have drawn unlimited attention among scientific investigators for therapeutic and diagnostic applications, due to their least toxicity, biodegradable nature, and low cost. ZnO-NPs can securely be used as medicine, preservative in food processing and packaging, and an antimicrobial mediator. They effortlessly disseminate into the food material, execute the microbes, and prevent a human being from dropping ill.

Doping, which consists of the intentional incorporation of impurities into host lattices, is the most commonly used

Received: February 1, 2022
Accepted: March 4, 2022
Published: March 15, 2022
method to tune nanomaterials’ optical and chemical properties. Amusingly, ZnO-NPs are testified by several studies as nontoxic to human cells and stable at very high temperatures, harmful to microorganisms, and having good biocompatibility to human cells; these facets required their usage as antibacterial agents. However, undoped ZnO-NPs have a higher optical bandgap energy (3.37 eV) and poor photocatalytic and antimicrobial activities. It is indispensable to alter ZnO-NPs to employ a major percentage of sunlight and boost the optical properties of ZnO-NPs. Certainly, this enhancement is due to the limitation of the countable ZnO-NPs drawbacks such as the wide bandgap, electron–hole recombination, and lack of visible light absorption/limited use of sunlight as a natural source. There are no strong descriptions of the mechanisms of bandgap widening in nanostructured ZnO outside the presence of vacancies as suggested by some researchers. Improving the photocatalytic and antibacterial action of metal oxide semiconductors by lessening the optical bandgap to mark potential absorption in the visible region and to impede the recombination of photogenerated electron–hole pairs has become a burning issue among scientists in recent years. Doping of wide-ranging bandgap metal oxides with diverse elements was recommended to overcome these drawbacks and shift their optical and chemical properties of ZnO-NPs. Certainly, this enhancement is due to the limitation of the countable ZnO-NPs drawbacks such as the wide bandgap, electron–hole recombination, and lack of visible light absorption/limited use of sunlight as a natural source. Improving the photocatalytic and antibacterial action of metal oxide semiconductors by lessening the optical bandgap to mark potential absorption in the visible region and to impede the recombination of photogenerated electron–hole pairs has become a burning issue among scientists in recent years. Doping of wide-ranging bandgap metal oxides with diverse elements was recommended to overcome these drawbacks and shift their optical and chemical properties of ZnO-NPs. Certainly, this enhancement is due to the limitation of the countable ZnO-NPs drawbacks such as the wide bandgap, electron–hole recombination, and lack of visible light absorption/limited use of sunlight as a natural source. Improving the photocatalytic and antibacterial action of metal oxide semiconductors by lessening the optical bandgap to mark potential absorption in the visible region and to impede the recombination of photogenerated electron–hole pairs has become a burning issue among scientists in recent years.

2. MATERIALS AND METHODS

To investigate the consequence of synthesizing temperature and sulfur doping on the bandgap energy of ZnO-NPs, ZnO-NPs were prepared by a sol–gel technique at different temperatures and mixed with different amounts of ZnS. The sol–gel procedure involves the conversion of a solution system of a liquid sol into a solid gel phase. The sol–gel technique is a favorite for the advantages of its repeatability, controllability of compositions, and simplicity in processing.

2.1. Chemicals and Instruments. Chemicals like hydrated zinc acetate (Zn(CH3COO)2·2H2O) ≥ 98% (Loba Chemie Pvt. Ltd.), sodium hydroxide (NaOH) ≥ 98% (Blulux Laboratories Ltd., 121005), ethanol (CH3COOH), and zinc sulfide (ZnS) 98% (Chemicals UDYO, 121001 (India)) were used in the research work. ZnS was used as a sulfur source for doping.

Figure 1. Schematic representations of the synthesis procedures of ZnO nanoparticles by the sol–gel process and their antibacterial activity.
Cu Kα radiation over a 2θ in the range of 30–70°. Absorbance measurements were conducted with a UV–visible spectrophotometer for the determination of bandgap energies. The FTIR analysis was also done to detect the various characteristic functional groups associated with the synthesized nanoparticles.

3. RESULTS AND DISCUSSION

ZnO nanopowder was obtained successfully by the sol–gel technique. The color of zinc oxide was changed from white to yellow upon heating and returns to white on cooling in open air. The comprehensive hydrolysis of Zn(CH₃COO)₂ with the support of NaOH in ethanol should result in the formation of a ZnO colloid. Attributable to the heating, Zn(CH₃COO)₂ within the solution undertakes hydrolysis developing acetate ions and zinc ions. The profusion of electrons in the oxygen creates the hydroxyl groups (–OH) of alcohol molecules to form bonds with the zinc ions. Zinc hydroxide acetate is a midway (an intermediate) product of the hydrolysis reaction, formed in the presence of H₂O and OH⁻ ions. The intermediate could be straightforwardly converted into ZnO at higher temperatures and through prolonged refluxing. NaCH₃COO is water-soluble and could therefore be separated easily from the end product.28 At the time of drying, Zn(OH)₂ is completely converted into ZnO. The total chemical reaction to form ZnO nanopowder is specified as follows:

\[
(Zn(CH₃COO)₂ \cdot 2H₂O (aq) + 2NaOH (aq) → Zn(OH)₂ (s) + 2NaCH₃COO (aq) + 2H₂O (l))
\]

\[
Zn(OH)₂ (s) \xrightarrow{\text{heat}} ZnO (s) + H₂O (g)
\]

\[
\text{constant stirring} \quad \text{Titratin} \quad \text{CH₃CH₂OH}
\]

\[
2 \text{Zn(CH₃COO)₂} + 2NaOH \rightarrow 2H₂O + ZnO \quad \text{(aq)}
\]

As a result of the huge electronegativity and size variation among S and O, sulfur doping is one of the best ways to modify the structural and optical properties of ZnO.22 Sulfur integration in ZnO-NPs is anticipated to modify the host optical character, which induces an intragap state. Further integration in ZnO-NPs is anticipated to modify the host imperfections.27

**RESULTS AND DISCUSSION**

The particles have a high crystallinity at a high temperature, 800 °C, which was clarified by a sharp peak and the highest intensity. It can be seen that the particles formed are ZnO nanoparticles and the crystallinity of the particles is amplified with the increased annealing temperature. This is caused by the fact that the leading higher diffusion rate at a high temperature resulted in the increased growth rate of ZnO crystals. The progression of larger crystals from those of smaller size leads to a reduction in the number of smaller particles, while larger particles continue to grow.29

At the time of drying, Zn(OH)₂ is completely converted into ZnO. The total chemical reaction to form ZnO nanopowder is specified as follows:

\[
(Zn(CH₃COO)₂ \cdot 2H₂O (aq) + 2NaOH (aq) \rightarrow Zn(OH)₂ (s) + 2NaCH₃COO (aq) + 2H₂O (l))
\]

\[
Zn(OH)₂ (s) \xrightarrow{\text{heat}} ZnO (s) + H₂O (g)
\]

\[
\text{constant stirring} \quad \text{Titratin} \quad \text{CH₃CH₂OH}
\]

\[
2 \text{Zn(CH₃COO)₂} + 2NaOH \rightarrow 2H₂O + ZnO \quad \text{(aq)}
\]

As a result of the huge electronegativity and size variation among S and O, sulfur doping is one of the best ways to modify the structural and optical properties of ZnO.22 Sulfur integration in ZnO-NPs is anticipated to modify the host optical character, which induces an intragap state. Furthermore, S is able to syndicate either through the component elements of the host (zinc and oxygen) or per impurities present in the sample (e.g., hydrogen), generating several different intermediate segments, such as SO₂, S₂O, H₂S, H₂SO₃, and ZnSO₄, which directs to undesired structural imperfections.

ZnO nanoparticles were synthesized from precursor Zn-(CH₃COO)₂·2H₂O by the conventional sol–gel process. The obtained products were calcined at temperatures of 500, 600, 700, and 800 °C for 3 h, and then, the products were characterized employing Cu Kα radiation over a 2θ in the range of 30–70°. The XRD patterns of the produced products are revealed in Figure 2a, which indicates the crystalline arrangement under the hexagonal structure (JCPDS card no. 01-080-0074) with leading peaks at 2θ = 31.87°, 34.36°, 36.2°, 47.5°, 56.53°, 62.75°, 66.35°, 67.85°, and 68.99°. These lines were indexed correspondingly as (100), (002), (101), (102), (110), (103), (112), and (201) and matched to the hexagonal phase of ZnO. Increasing the annealing temperature can increase the reaction rate of decomposition of precursors due to the bonds in precursors being broken by the heat energy at high temperatures.

The particles have a high crystallinity at a high temperature, 800 °C, which was clarified by a sharp peak and the highest intensity. It can be seen that the particles formed are ZnO nanoparticles and the crystallinity of the particles is amplified with the increased annealing temperature. This is caused by the fact that the leading higher diffusion rate at a high temperature resulted in the increased growth rate of ZnO crystals. The progression of larger crystals from those of smaller size leads to a reduction in the number of smaller particles, while larger particles continue to grow.29 This trend is possibly due to the evaporation of water molecules of the ZnO nanoparticles and the reorganization of the NPs. In this study, it was observed that there is a continuous increase in the particle size through increasing the temperature. The growth in the particle size is due to the smaller particles agglomerating or amalgamating into larger particles, which is a result of solid-state diffusion (an atomic migration from one point to another through the solid).

Figure 2b exhibits the XRD patterns of undoped and S-doped ZnO-NPs; the precise peaks were located at (2θ) = 31.87°, 34.36°, 36.2°, 47.5°, 56.53°, 62.75°, 66.35°, 67.85°, and 68.99°. The diffraction peaks of the S-doped ZnO-NPs are likewise in good agreement with those of hexagonal ZnO (JCPDS card no. 01-080-0074) and are almost identical to those of pure ZnO, indicating that the sulfur atoms have been doped in the ZnO crystal and no new peak has been formed due to sulfur.

It was perceived that the amounts of dopants affect the intensity of the diffraction peaks. A decrease in the intensity of doping is due to a change in electron density. Overall, the intensity of the diffraction peaks decreases greatly through the increase of dopant concentration, indicating a relative loss of crystallinity due to lattice alteration. When sulfur ions are amalgamated into the periodic crystal lattice of ZnO, a tension is induced into the system, following the alteration of the lattice periodicity and the decrease in crystal symmetry.29 Here, it is significant that the crystallinity of ZnO-NPs retained after doping and peak intensities decreased, indicating improved particle properties (Figure 2a,b).

For sulfur-doped ZnO-NPs, the structure was modeled by the replacement of a segment of the O⁻ by S²⁻. Thus, the ZnO-NPs appear to be significantly sulfur-doped. Zinc oxysulfides, ZnO₁₋ₓSₓ, are known to have a lower bandgap than ZnO due to the effect of band-bowing. If the sulfur doping were to be limited to an outer shell of each ZnO-NP, the resulting intermediate-stage NPs would consist of a shrunk ZnO core surrounded by a ZnS shell.29

The crystallite sizes of both pure and S-doped ZnO-NPs have been achieved from the full-width at half-maximum (FWHM) of the supreme strong peaks of the corresponding crystals using the Scherrer equation, \( D = \frac{0.92}{\beta \cos \theta} \), where \( \lambda \) is the
X-ray wavelength, $D$ is the average crystallite size, $\theta$ is Bragg’s diffraction angle, and $\beta$ is the FWHM in radians. The crystallite size calculated based on the XRD result (by using the Debye–Scherrer equation) was increased with the increasing intensity due to the temperature and decreased with the decreasing peak intensity due to the doping concentration (Table 1). The most noticeable tendency versus particle size is that the surface-to-volume ratio increases for smaller particles.29,30

The light absorption properties of ZnO-NPs synthesized at different temperatures were obtained with a UV−vis spectrophotometer in the wavelength range of 200−800 nm, which provides a double beam; one of the beams passes through a reference cell for system calibration, whereas the second beam passes via the sample. Finally, the absorbance spectrum of the sample versus the wavelengths was plotted. The UV−vis absorption spectrum of the synthesized ZnO-NPs at 500, 600, 700, and 800 °C is presented in Figure 3, which displays that the ZnO-NPs indicate an absorption peak in the UV range at 378, 379, 381, and 379 nm, respectively. After the annealing temperature is amplified, the absorption edge slightly shifted to higher wavelengths. This shift is due to the improvement of the crystallinity of the NPs.

The optical bandgap ($E_g$) was calculated using the Tauc method. Typically, $E_g$ for the synthesized ZnO-NPs could be obtained by plotting $(\alpha h \nu)^2$ versus $h \nu$, where $\alpha$ and $h \nu$ are the absorption coefficient and the photon energy, respectively. Values of log $A$, $h \nu$, and $(\alpha h \nu)^2$ were calculated to determine bandgap energies for entire samples and are given in the Supporting Information. Figure 4 displays plots of $(\alpha h \nu)^2$ versus photon energy for ZnO at various annealing temperatures. The estimated $E_g$ values for ZnO at 500, 600, 700, and 800 °C were 3.34, 3.3, 3.27, and 3.31 eV, respectively. The respective data from which the graphs in Figure 4 were sketched and the bandgaps were calculated are given in Tables S1−S4. The reduction in $E_g$ is achieved by increasing the annealing temperature. As the temperature increases, the amplitude of atomic vibrations increases, bringing about a larger interatomic spacing.3 We propose that the surprising difference in $E_g$ results from the internal strain parameters established within the ZnO-NPs at higher temperatures, as the particles become larger. The internal strains could be associated with the incidence of organic ligands chained to the growing NP surfaces resulting from the synthesis reaction.11

The S doping into ZnO-NPs intensifies the surface-to-volume ratio, which significantly enhances the visible light absorption. The absorbance in the stated wavelength range starting from 200 to 800 nm is improved upon S doping. Figure 5 shows that the maximum optical absorption was obtained for the largest dopant concentration (3.85%), while the minimum optical absorption was obtained for undoped ZnO nanoparticles. Thus, the more the dopant quantity, the greater the optical absorption obtained. As the wavelength of incident light declined to the ultraviolet region, the absorbance of S-doped ZnO-NPs amplified with a fundamental absorption edge at around 379 nm of wavelength. The absorption of the sulfur-doped ZnO-NPs at 0% (undoped), 0.99, 1.96, 2.91, and

Table 1. Calculated Crystalline Size of Synthesized ZnO-NPs at Different Synthetic Temperatures and Doping Concentrations

| S/N | synthesis condition | $\theta$ (Degree) | $\cos \theta$ | $\lambda$ (nm) | $h \nu$ (nm) | $\beta$ (radian) | $D$ (nm) |
|-----|---------------------|------------------|-------------|---------------|-------------|----------------|--------|
| 1   | ZnO at 500 °C       | 18.170           | 0.7778      | 0.154         | 0.066       | 1.63           |
| 2   | ZnO at 600 °C       | 18.170           | 0.7778      | 0.154         | 0.054       | 2.00           |
| 3   | ZnO at 700 °C       | 18.170           | 0.7778      | 0.154         | 0.048       | 2.23           |
| 4   | ZnO at 800 °C       | 18.170           | 0.7778      | 0.154         | 0.040       | 2.67           |
| 5   | 0.99% S/ZnO         | 18.170           | 0.7778      | 0.154         | 0.043       | 2.52           |
| 6   | 1.96% S/ZnO         | 18.170           | 0.7778      | 0.154         | 0.049       | 2.22           |
| 7   | 2.91% S/ZnO         | 18.170           | 0.7778      | 0.154         | 0.053       | 2.05           |
| 8   | 3.85% S/ZnO         | 18.170           | 0.7778      | 0.154         | 0.066       | 1.63           |

Figure 2. XRD patterns of ZnO-NPs (a) synthesized at different temperatures and (b) synthesized at varying dopant concentrations compared with undoped ZnO-NPs.

Figure 3. Ultraviolet−visible spectra of ZnO-NPs produced at different temperatures by the sol−gel method.
3.85% displays that the ZnO-NPs exhibit an absorption peak in the UV range at 319, 376, 376, 377, and 379 nm, respectively. The redshift (bathochromic shift), shift to longer $\lambda$, of the optical absorption edge must be related to the bandgap reduction led by the semiconductor−sulfur accompanied by the merging of the donor and conduction bands. The light absorbance spectra of ZnO-NPs demonstrate an improved visibility with higher dopant levels (dopant percentage composition). Normally, the quality of ZnO-NPs improved with the elevating dopant concentration. In a similar manner to the undoped one, the energy bandgaps of doped ZnO-NPs were also calculated from the UV−vis absorbance spectral values (Figure 6 and Tables S5−S8). Accordingly, the estimated optical bandgaps of doped ZnO-NPs for different doping concentrations (0, 0.99, 1.96, 2.91, and 3.85%) were 3.3, 3.06, 3.02, and 2.98 eV, respectively. The decrease in the bandgap observed is ascribed to the combined effect of synthesis temperature and sulfur doping (Figures 4 and 6).

The corresponding data from which the graphs in Figure 6 were sketched and the bandgaps for the doped ZnO-NPs were calculated are given in Tables S5−S8.

Light transmittance properties were measured for two randomly selected samples by FTIR (Perkin Elmer Spectrum two) in the wavenumber range of 4000−400 cm$^{-1}$. Figure 7 shows the IR spectra of ZnO-NPs synthesized at 600 °C and 0.99% (S/ZnO) samples in order to see their difference in functional groups. The IR spectra prove that the zinc oxide absorption band with a stretching mode of Zn−O is between 400 and 850 cm$^{-1}$, which corresponds to the hexagonal ZnO crystal structure.25 Peaks sandwiched between 2730 and 3050 cm$^{-1}$ are due to the C−H stretching vibration of alkane groups. The peaks observed between 1720 and 1300 cm$^{-1}$ are due to the asymmetrical and symmetrical stretching of the zinc carboxylate, which comes from reactive carbon-containing plasma species during synthesis. These observations from the FTIR bands indicated the existence of impurities mainly near ZnO surfaces. In addition, there is a strong absorption peak observed at 900 cm$^{-1}$ in both samples assigned to Zn−O. A new peak, which is not sharp, was observed at 1498 cm$^{-1}$ due to microstructure formation of the sample (Zn−S) during doping.31 The broadband at 3500 cm$^{-1}$ is assigned to the O−H stretching mode of the hydroxyl group. The peak at 1310 cm$^{-1}$ corresponds to a CH$_3$ bending vibration.32,33 The hydroxyl group resulted from the hygroscopic nature of ZnO.23 ZnO-NPs appear to be significantly sulfur-doped. Zinc oxysulfides, ZnO$_{1−x}$S$_x$, are recognized to possess a lower bandgap than ZnO as a result of the effect of band-bowing.30

A pure culture of S aureus was obtained from Mettu Karl Referral Hospital and activated in the Biology Laboratory of Mettu University for antibacterial activity tests. In this study, 0.1 g of ZnO-NPs of different doping concentrations and different synthesizing temperatures were prepared in 1000 μL
of distilled water. Interaction among NPs and the cell wall is adequate to cause toxicity. If it is precise, formerly sufficient amounts of MO-NPs are needed so that the bacterial cells are entirely enveloped and shielded from their environment withdrawing no chance for nutrition to be engaged to continue the life process. It is comprehensively recognized that ZnO-NPs are antibacterial agents and inhibit the growth of microorganisms by pervading into the cell membrane.19

The zone of inhibition test method was selected for the antibacterial test. The advantages of this method are the test simplicity that does not require any special equipment and the easier cost for testing. Employing a sterile swab, a suspension of the pure culture was spread uniformly over the face of a sterile agar plate. Figure 8 shows the antibacterial agent applied; the agar plate was incubated for 24 h, at a temperature suitable for the test of the microorganism. The antibacterial agent leached from the object into the agar and then exercised a growth-inhibiting effect; at that point, a vibrant zone (the zone of inhibition) appeared about the test product. The zone of inhibition was measured after 24 h of incubation. The antibacterial activity of ZnO could be reliant on the presence of standard visible light.18,31 The magnitude of the zone of inhibition is habitually correlated with the level of antimicrobial activity present in the sample or product; a larger zone of inhibition indicated a more effective antibacterial property.

Figure 6. Bandgap energies of doped ZnO nanoparticles: (a) undoped, (b) 0.99% S/ZnO, (c) 1.96% S/ZnO, (d) 2.91% S/ZnO, and (e) 3.85% S/ZnO.

Figure 7. FTIR bands of undoped and 0.99% S/ZnO-NP samples.

Figure 8. Zone of inhibition test for the antibacterial activity of ZnO.
inhibition usually means that the antibacterial activity is more potent (Figure 8).

The antibacterial activity increased as the calcination temperature increased and as a function of sulfur loading contents because of a reduction of the bandgap energy of ZnO-NPs. This has a consistent explanation with the hypothesis that ZnO-NPs with a smaller bandgap energy have a superior antibacterial activity against S. aureus. In ZnO-NPs, a significant number of excitons exist, but due to their wider bandgap, only a few electron–hole pairs could be created at room temperature. This important effect determines the antibacterial activity of NPs. Table 2 shows the ZnO-NP synthesis conditions, bandgap energies, crystallite sizes, and diameters of inhibition zones.

| S/N | synthesis condition | bandgap energy (eV) | crystallite size (nm) | inhibition zone (cm) |
|-----|---------------------|---------------------|----------------------|----------------------|
| 1   | ZnO at 500 °C       | 3.340               | 1.630                | 1.401                |
| 2   | ZnO at 600 °C       | 3.300               | 2.002                | 1.600                |
| 3   | ZnO at 700 °C       | 3.220               | 2.230                | 2.100                |
| 4   | ZnO at 800 °C       | 3.110               | 2.674                | 2.000                |
| 5   | 0.99% S/ZnO         | 3.060               | 2.515                | 1.700                |
| 6   | 1.96% S/ZnO         | 3.050               | 2.216                | 2.100                |
| 7   | 2.91% S/ZnO         | 3.020               | 2.056                | 2.200                |
| 8   | 3.85% S/ZnO         | 2.980               | 1.626                | 2.400                |

4. CONCLUSIONS

In the present work, the impact of varied sulfur doping concentrations and different synthesis temperatures on the optical bandgap energy and the additionally crystalline structure of ZnO-NPs, grown by the sol–gel method, was studied and discussed. The XRD results showed similar patterns with many published literature XRD patterns in which ZnO nanoparticles have a hexagonal unit cell structure. From the XRD results, it was observed that as the temperature increased, the crystallinity and particle size were increased. This could be attributed to governing a higher diffusion rate at a high temperature, which resulted in an enhanced growth rate of ZnO crystals. On the other hand, crystallinity and crystallite size were decreased with the sulfur loading. The UV absorption spectra showed redshifts from 378 toward 379 nm and 319 toward 379 nm due to the calcination temperature and doping with sulfur, respectively. Generally, the bandgap energy was decreased from 3.34 to 3.22 eV with increasing calcination temperatures and decreased from 3.06 to 2.98 eV with increasing sulfur doping concentrations. In addition, doping decreased the particle size and increased the stability. As a result of the combined effects, the antibacterial activity of the doped ZnO-NPs was dramatically improved and reached 2.4 cm compared to the undoped ZnO-NPs (@ 600 °C), which is 1.6 cm. Thus, this investigation remarks that sulfur-doped ZnO-NPs could inhibit bacterial growth if incorporated into a film and used in the desired application.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.2c00647.

Calculated values of log A, absorption coefficient (α), photon energy (hν), and (αhν)2 for ZnO-NPs at temperatures of 500, 600, 700, and 600 °C (Tables S1–S4) and sulfur-doped ZnO-NPs with 0.99% S/ZnO, 1.96% S/ZnO, 2.91% S/ZnO, and 3.85% S/ZnO (Tables S5–S8) (PDF)

AUTHOR INFORMATION

Corresponding Author
Tamene Tadesse Beyene — Department of Chemistry, College of Natural Sciences, Jimma University, Jimma 251, Ethiopia; orcid.org/0000-0002-1096-5557; Phone: +251917822252; Email: tamene.tadesse@ju.edu.et

Authors
Kenassa Wagkari Aga — Department of Chemical Engineering, College of Technology, Mettu University, Mettu 251, Ethiopia
Mulugeta Tesema Efá — Department of Chemistry, College of Natural Sciences, Dambi Dollo University, Jimma 251, Ethiopia

Complete contact information is available at:
https://pubs.acs.org/10.1021/acsomega.2c00647

Author Contributions
T.T.B. drew the scheme in Figure 1 and the graphical abstract, and K.W.A. took and labeled pictures in Figure 7.

Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors are highly grateful for the financial support from Mettu University, Mettu-Oromiya, Ethiopia.

REFERENCES

(1) Oskam, G.; Penn, R. L.; Hu, Z.; Searson, P. C. Synthesis and Characterization of Metal Oxide Nanoparticles. Emerging Fields in Sol-Gel Science and Technology, López, T. M.; Añón, D.; Aegerter, M.; Springer: Boston, MA, 2003.
(2) Yusuf, M. Silver Nanoparticles: Synthesis and Applications. Handbook of Ecomaterials; Springer: Cham, Switzerland, 2018; pp 2343–2356.
(3) Chavali, M. S.; Nikolova, M. P. Metal oxide nanoparticles and their applications in nanotechnology. SN Appl. Sci. 2019, 1, 607.
(4) Rastogi, A.; Zivcak, M.; Shtar, O.; Kalaji, H. M.; He, X.; Mbarki, S.; Brestic, M. Impact of Metal and Metal Oxide Nanoparticles on Plant: A Critical Review. Front. Chem. 2017, 5, No. 78.
(5) Nguyen, N. H. A.; Padil, V. T. T.; Slaveykova, V. I.; Černik, M.; Čevcu, A. Green Synthesis of Metal and Metal Oxide Nanoparticles and Their Effect on the Unicellular Alga Chlamydomonas reinhardtii. Nanoscale Res. Lett. 2018, 13, 159.
(6) Tsuzuki, T. Mechanochemical synthesis of metal oxide nanoparticles. Commun. Chem. 2021, 4, 143.
(7) Beyene, T. T.; Bezbah, H. K.; Weret, M. A.; Hagos, T. M.; Huang, C.-J.; Wang, C.-H.; Su, W.-N.; Dai, H.; Hwang, B.-J. Concentrated Dual-Salt Electrolyte to Stabilize Li Metal and Increase Cycle Life of Anode Free Li-Metal Batteries. J. Electrochem. Soc. 2019, 166, A1501–A1509.
(8) Seabra, A. B.; Durán, N. Nanotoxicology of Metal Oxide Nanoparticles. Metals 2015, 5, 934–975.
(9) Dür, M.; Rosselli, S.; Yasuda, A.; Nelles, G. Band-Gap Engineering of Metal Oxides for Dye-Sensitized Solar Cells. J. Phys. Chem. B 2006, 110, 21899–21902.
The proposal of a unified methodology to its determination. Sci. Rep. 2019, 9, 11225.

Samriti; Rajput, V.; Gupta, R. K.; Prakash, J. Engineering metal oxide semiconductor nanostructures for enhanced charge transfer: fundamentals and emerging SERS applications. J. Mater. Chem. C 2022, 10, 73–95.

Yamamoto, O.; Komatsu, M.; Sawai, J.; Nakagawa, Z.-E. Effect of lattice constant of zinc oxide on antibacterial characteristics. J. Mater. Sci. Mater. Med. 2004, 15, 847–851.

Alswat, A. A.; Ahmad, M. B.; Saleh, T. A. Preparation and Characterization of Zeolite\(\text{Zinc Oxide-Copper Oxide Nanocomposite: Antibacterial Activities. Colloid Interface Sci. Commun. 2017, 16, 19–24.}

Alswat, A. A.; Ahmad, M. B.; Hussein, M. Z.; Ibrahim, N. A.; Saleh, T. A. Copper oxide nanoparticles-loaded zeolite and its characteristics and antibacterial activities. J. Mater. Sci. Technol. 2017, 33, 889–896.

Fernandez-Lima, F. A.; Becker, C.; McKenna, A. M.; Rodgers, R. P.; Marshall, A. G.; Russell, D. H. Petroleum Crude Oil Characterization by IMS-MS and FTICR MS. Anal. Chem. 2009, 81, 9941–9947.

Zhang, Y.; Nayak, T. R.; Hong, H.; Cai, W. Biomedical applications of zinc oxide nanomaterials. Curr. Mol. Med. 2013, 13, 1633–1645.

Saleh, T. A. Protocols for synthesis of nanomaterials, polymers, and green materials as adsorbents for water treatment technologies. Environ. Technol. Innovation 2021, 24, No. 101821.

Jiang, J.; Pi, J.; Cai, J. The Advancing of Zinc Oxide Nanoparticles for Biomedical Applications. Bioinorg. Chem. Appl. 2018, No. 1062562.

Siddiqui, K. S.; ur Rahman, A.; Tajuddin; Husen, A. Properties of Zinc Oxide Nanoparticles and Their Activity Against Microbes. Nanoscale Res. Lett. 2018, 13, 141.

Saleh, T. A. Characterization, determination and elimination technologies for sulfur from petroleum: Toward cleaner fuel and a safe environment. Trends Environ. Anal. Chem. 2020, 25, No. e00080.

Rajeshkumar, S.; Sandhiya, D. Biomedical Applications of Zinc Oxide Nanoparticles Synthesized Using Eco-friendly Method. In Nanoparticles and their Biomedical Applications; Shukla, A. K., Ed.; Springer: Singapore, 2020; pp 65–93.

Shaba, E. Y.; Jacob, J. O.; Tijani, J. O.; Suleiman, M. A. T. A critical review of synthesis parameters affecting the properties of zinc oxide nanoparticle and its application in wastewater treatment. Appl. Water Sci. 2021, 11, 48.

Ss, K.; Kumar, A. Potential risks and benefits of zinc oxide nanoparticles: a systematic review. Crit. Rev. Toxicol. 2020, 50, 47–71.

Hasmidawani, J. N.; Azlina, H. N.; Norita, H.; Bonnia, N. N.; Ratim, S. Synthesis of ZnO Nanorods Using Sol-Gel Method. Procedia Chem. 2016, 19, 211–216.

Fabbri, F.; Nasi, L.; Fedeli, P.; Ferro, P.; Salvati, G.; Mosca, R.; Calzolari, A.; Catellani, A. S-induced modifications of the optoelectronic properties of ZnO mesoporous nanobelts. Sci. Rep. 2016, 6, 27948.

Rehman, W.; Bhat, A. H.; Sulaimon, A.; Khan, I.; Ullah, H. Effect of volumetric concentration of MWCNTs on the stability and thermal conductivity of nanofluids. Crit. Rev. Toxicol. 2016, 1787, No. 050029.

Hasmidawani, J. N.; Azlina, H. N.; Norita, H.; Bonnia, N. N.; Ratim, S.; Ali, E. S. Synthesis of ZnO Nanorods Using Sol-Gel Method. Procedia Chem. 2016, 19, 211–216.

Xiong, G.; Pal, U.; Serrano, J. G.; Ucer, K. B.; Williams, R. T. Photoluminescence and FTIR study of ZnO nanoparticles: The Impurit and defect perspective. Phys. Status Solidi C 2006, 3, 3577–3581.