

**ARTICLE**

# Green Synthesis and Characterization of ZnS and ZnS@Ag<sub>2</sub>S Core–Shell Nanoparticles Using Mint Leaf Extract

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**ABSTRACT:** In this study, zinc sulfide nanoparticles (ZnS NPs) and zinc sulfide @ Silver sulfide core-shells (ZnS@Ag<sub>2</sub>S NPs) were prepared using the green method with mint leaf extract as a reducing and coating agent, at varying concentrations of silver nitrate (AgNO<sub>3</sub>) (0.005, 0.01, and 0.02 M). X-ray diffraction analysis (XRD) results showed the formation of a cubic phase of ZnS NPs and a monoclinic phase of Ag<sub>2</sub>S with increasing silver nitrate concentration. The average crystalline size of ZnS NPs was calculated to be 2.01 nm and (2.78, 2.65, and 2.13 nm) after Ag<sub>2</sub>S formation, while the shell (Ag<sub>2</sub>S) was found to be (7.47, 5.89, and 3.83 nm). Transmission Electron Microscopy (TEM) analysis revealed the formation of an Ag<sub>2</sub>S shell around ZnS, with the shell becoming more uniform at the silver nitrate concentration (0.01 M). Energy Dispersive X-Ray (EDX) analysis showed the presence of the core's main elements, zinc and sulfur, and an increase in silver (Ag) content with increasing silver nitrate concentration in the core-shells. Fourier Transform Infrared Analysis (FTIR) results showed vibrational frequencies belonging to the organic compounds of the plant extract, in addition to the appearance of zinc-sulfur bonds and peaks between 450 and 900 cm<sup>-1</sup> indicating S-Ag-related vibrations. Finally, UV-Visible results showed an improvement in UV absorption capacity with increasing silver nitrate concentration. The optical energy gap of ZnS NPs was approximately 3.77 eV, while it was 3.61, 3.72, and 3.74 eV for ZnS@Ag<sub>2</sub>S NPs at different concentrations of silver nitrate (0.005, 0.01, and 0.02 M), respectively.

**KEYWORDS:** Green method; mint leaf extract; zinc sulfide nanoparticles; zinc sulfide @ silver sulfide core-shells NPs

## 1 Introduction

Nanotechnology is one of the most prominent scientific fields, having experienced significant progress in recent decades [1,2]. It focuses on the study and synthesis of materials at the nanoscale, ranging from 1 to 100 nm [3]. Through this technology, we have been able to access new materials and properties that were not available in traditional materials, contributing to the development of a wide range of applications in fields such as electronics, medicine, renewable energy, and sensing [4]. One of the materials that has garnered significant attention in this context is zinc sulfide (ZnS) nanoparticles. ZnS is a promising material from the second and fifth groups of the periodic table, typically found in two structures: zinc blend and wurtzite, with direct energy gaps of 3.54 eV and 3.91 eV, respectively [5]. ZnS NPs exhibit distinct properties compared to their bulk counterparts due to their surface-to-volume ratio, these nanoparticles can be synthesized using a variety of physical and chemical methods, though some methods have certain limitations [6]. As a result, green synthesis methods are considered an environmentally friendly, simple, and cost-effective alternative [7]. ZnS NPs have been widely explored for diverse applications, including bioimaging [8], skin

regeneration [9], dye degradation [10], catalysis [11], electronic devices [12], sensing and optoelectronic technologies [13]. Nanoparticle coating is a method used to enhance the optical and chemical properties of nanomaterials by adding an outer layer to the surface of the nanoparticles, the core-shell system is an innovative design where the core is made of a nanomaterial such as zinc sulfide, while the shell is made of another material such as silver sulfide ( $\text{Ag}_2\text{S}$ ) [14]. Silver sulfide contributes to enhanced stability and improved light absorption, making these particles more effective in photovoltaic applications such as solar cells and light-emitting devices [15,16].

This research aims to use a novel method for preparing zinc sulfide nanoparticles as a core, coating them with silver sulfide as a shell, using mint leaf extract as a reducing agent and coating the nanoparticles, and then studying their structural, morphological, and optical properties for suitable applications.

## 2 Methodology

### 2.1 Materials Employed in the Preparation

Mint leaves purchased from local markets, Zinc nitrate  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (HiMedia Laboratories Pvt. Ltd., India, 99–100%), Sodium sulfide  $\text{Na}_2\text{S} \cdot x\text{H}_2\text{O}$  (Daryaganj, Delhi, India), Silver nitrate (CDH, India, 99.9%), Deionized water (DW) and ethanol (96%).

### 2.2 Preparation of Zinc Sulfide Nanoparticles

Zinc nitrate  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  with (0.2 M) was dissolved in 50 mL of deionized water, then 30 mL of mint leaf extract was prepared by taking 10 g of dried leaves and adding 250 mL of DW to them was added dropwise to the solution. Then, sodium sulfide  $\text{Na}_2\text{S} \cdot x\text{H}_2\text{O}$  at (0.2 M) dissolved in 50 mL of deionized water is added to the mixture with continuous stirring for one hour at room temperature. The resulting precipitate was separated by centrifugation at 4000 rpm for 30 min and then washed three times, twice with DW and once with ethanol for 30 min, and left to air dry overnight at room temperature.

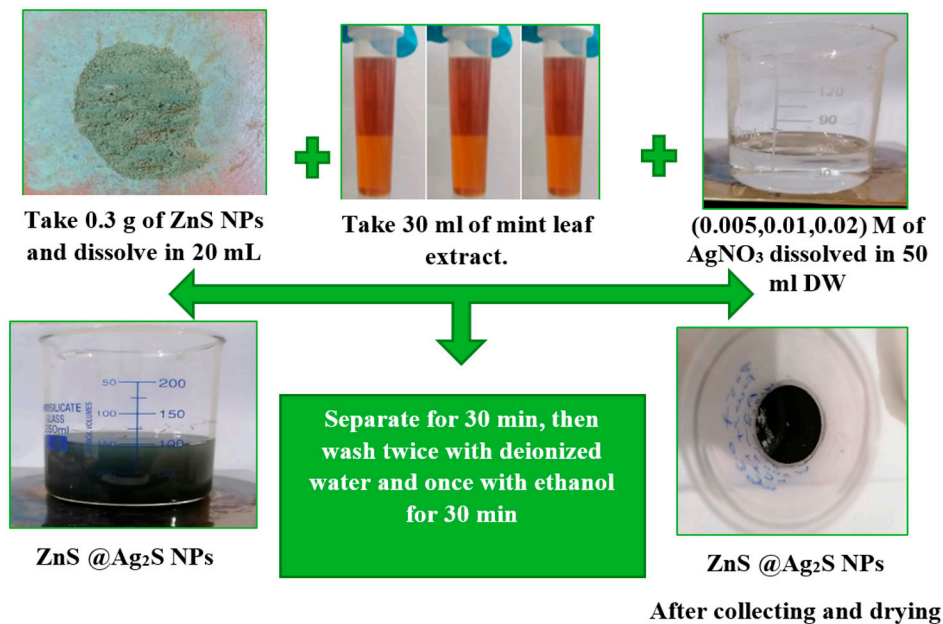
### 2.3 Preparation of ZnS@Ag<sub>2</sub>S Core–Shell NPs

0.3 g of the previously prepared ZnS NPs were weighed and 20 mL of DW was added, followed by mixing using a magnetic stirrer for approximately 15 min. After that, 30 mL of mint leaf extract was added dropwise and then concentrations of silver nitrate (0.005, 0.01, 0.02) M dissolved in 50 mL of DW were added. The reaction was left with continuous stirring for an hour. The precipitate was separated and washed twice with DW and once with ethanol for 30 min. The precipitate was left to dry overnight at room temperature and the resulting precipitate was black. Fig. 1 shows the steps for preparing ZnS@Ag<sub>2</sub>S.

### 2.4 Characterization Techniques

XRD pattern of ZnS NPs and ZnS@Ag<sub>2</sub>S NPs were recorded using an Aeris Research Edition X-ray diffractometer (Malvern Panalytical) equipped with  $\text{Cu K}\alpha$  ( $\lambda = 0.154$  nm) radiation. The instrument provides a high angular resolution of less than  $0.04^\circ$  ( $2\theta$ ), enabling accurate phase identification and crystallite size estimation. The particles morphology was examined by (TEM) PHILIPS, CM120, The Netherland. EDX analysis was performed using a Thermo Scientific™ Axia™ ChemiSEM (Thermo Fisher Scientific) to examine the elemental composition of the synthesized nanoparticles. The properties related to the functional groups on the surface in addition to the chemical bonds of the basic elements have been examined by FTIR analysis (Perkin Elmer TWO, USA), the spectra have been scanned in range ( $4000$ – $400$   $\text{cm}^{-1}$ ) at resolution ( $0.5$   $\text{cm}^{-1}$ ). The optical absorbance spectrum was measured using a Shimadzu UV-1800 spectrophotometer

(the wavelength ranging from 190–1100 nm). In addition, the particle size distribution was determined from TEM micrographs by measuring the diameter of 20 individual nanoparticles using ImageJ software.



**Figure 1:** The steps for preparing ZnS@Ag<sub>2</sub>S core-shell NPs using the green method.

### 3 Results and Discussion

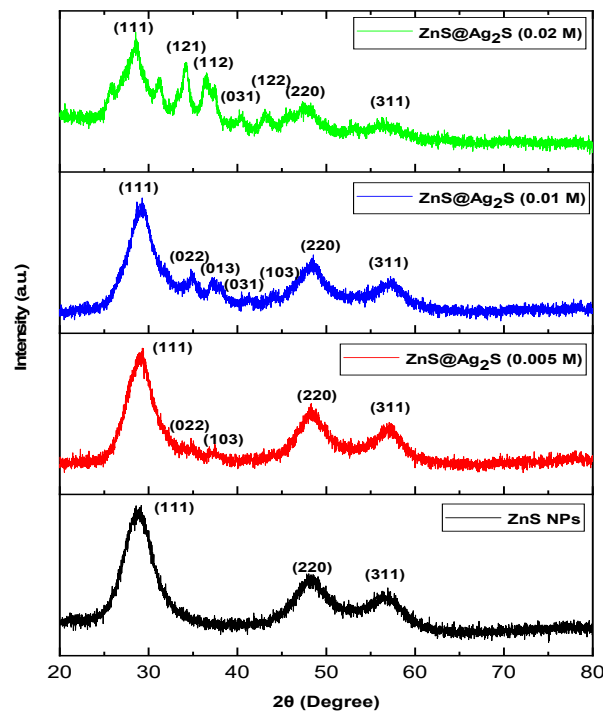
#### 3.1 X-Ray Diffraction Analysis for ZnS NPs and ZnS@Ag<sub>2</sub>S NPs Prepared Using Mint Leaf Extract

XRD analysis was performed to analyze the crystal structure and phase purity of ZnS NPs and ZnS@Ag<sub>2</sub>S NPs which were prepared using mint leaf extract with different concentrations of silver nitrate (0.005, 0.01, and 0.02 M), as shown in Fig. 2. The XRD results showed the ZnS NPs exhibited a cubic phase and polycrystalline nature with peaks at  $2\theta = 29.16^\circ$  (hkl = 111),  $2\theta = 48.02^\circ$  (hkl = 220), and  $2\theta = 56.92^\circ$  (hkl = 311), correspond to JCPDS card (5-566) [17]. While XRD results for ZnS@Ag<sub>2</sub>S NPs showed that the cubic phase of ZnS NPs appeared at  $2\theta = 29.3014^\circ$  (hkl = 111),  $2\theta = 48.3094^\circ$  (hkl = 220), and  $2\theta = 57.0874^\circ$  (hkl = 311) at a concentration of 0.005 M, and at  $2\theta = 29.2794^\circ$  (hkl = 111),  $2\theta = 48.3094^\circ$  (hkl = 220), and  $2\theta = 57.0874^\circ$  (hkl = 311), at a concentration of 0.01 M, and at  $2\theta = 28.5314^\circ$  (hkl = 111),  $2\theta = 47.3194^\circ$  (hkl = 220), and  $2\theta = 56.2294^\circ$  (hkl = 311), at a concentration of 0.02 M, while peaks appeared at  $2\theta = 34.7684^\circ$  (hkl = 022) and  $2\theta = 37.4524^\circ$  (hkl = 103), reverts to Ag<sub>2</sub>S in the monoclinic phase, but with low intensity at a concentration of 0.005 M [18]. As the silver nitrate concentration increased to 0.01 M and 0.02 M, an increase in the intensity of the monoclinic peaks was observed, along with the appearance of new peaks for Ag<sub>2</sub>S at  $2\theta = 40.4664^\circ$  (hkl = 031), and  $2\theta = 44.0634^\circ$  (hkl = 103) for 0.01 M and  $2\theta = 40.2244^\circ$  (hkl = 031), and  $2\theta = 43.0954^\circ$  (hkl = 122) for 0.02 M, correspond to JCPDS card (14-0072) [19]. These changes indicate that increasing the silver nitrate concentration contributed to improved crystallization and enhanced silver sulfide formation in the monoclinic phase, which is in agreement with [20].

Also, the average crystalline size was calculated using Scherrer's equation Eq. (1) [21,22], where it was found for ZnS NPs 2.01 nm. However, after the formation of Ag<sub>2</sub>S NPs at a shell, an increase in the crystal size of the ZnS was observed, reaching to (2.78, 2.65, and 2.13 nm) for the concentration of silver nitrate (0.005, 0.01, and 0.02 M), respectively. The change in ZnS nanocrystal size during the formation of ZnS@Ag<sub>2</sub>S NPs is attributed to the structural interaction between the two phases and the differential

crystal structures of the two phases, leading to lattice mismatch and the generation of crystallographic stress at the interface [23]. As for the  $\text{Ag}_2\text{S}$ , it was observed that the average crystal size decreases with increasing concentration of silver nitrate, where it was (7.47, 5.89, and 3.83 nm) for (0.005, 0.01 and 0.02 M), respectively, this decrease is may be due to the rapid reaction between silver ions ( $\text{Ag}^+$ ) and sulfur ions ( $\text{S}^{2-}$ ) which leads to rapid saturation of the ZnS surface with  $\text{Ag}_2\text{S}$ , thus reducing the opportunity for crystal growth in the shell [24]. Furthermore, the change in the values of the interfacial distances ( $d_{hkl}$ ) indicates the occurrence of internal network distortions resulting from the strong interaction between the two phases [25]. Table 1 shows the structural parameters of ZnS NPs and ZnS@ $\text{Ag}_2\text{S}$  core-shell NPs.

$$D = K \lambda / \beta \cos\theta \quad (1)$$



**Figure 2:** Represent to XRD pattern of ZnS NPs and ZnS@ $\text{Ag}_2\text{S}$  NPs with different concentrations of  $\text{AgNO}_3$  (0.005, 0.01, and 0.02 M).

**Table 1:** The structural parameters of ZnS NPs and ZnS@ $\text{Ag}_2\text{S}$  core-shell NPs with varying concentrations of  $\text{AgNO}_3$  (0.005, 0.01 and 0.02) M.

Samples	$2\theta$ (Deg.)	FWHM (Deg.)	$d_{hkl}$ Exp. (Å)	C.S (nm)	hkl	Phase
ZnS NPs	29.1644	4.03072	3.0596	2.04	(111)	Cub. ZnS
	48.0184	4.44872	1.8932	1.96	(220)	Cub. ZnS
	56.9174	4.40746	1.6165	2.05	(311)	Cub. ZnS
ZnS @ $\text{Ag}_2\text{S}$ 0.005 M	29.3014	3.35875	3.0456	2.45	(111)	Cub. ZnS
	48.3094	3.39219	1.8824	2.57	(220)	Cub. ZnS
	57.0874	2.68195	1.6121	3.37	(311)	Cub. ZnS
	34.7684	1.03906	2.5782	8.02	(022)	Monoclinic $\text{Ag}_2\text{S}$
	37.4524	1.21197	2.3993	6.92	(103)	Monoclinic $\text{Ag}_2\text{S}$

**Table 1: Cont.**

Samples	2 $\theta$ (Deg.)	FWHM (Deg.)	$d_{hkl}$ Exp. (Å)	C.S (nm)	hkl	Phase
ZnS @ Ag <sub>2</sub> S 0.01 M	29.2794	3.30484	3.0478	2.49	(111)	Cub. ZnS
	48.5404	3.0884	1.8740	2.82	(220)	Cub. ZnS
	57.2304	3.41762	1.6084	2.65	(311)	Cub. ZnS
	34.7574	1.82362	2.5790	4.57	(022)	Monoclinic Ag <sub>2</sub> S
	37.1334	1.95158	2.4192	4.30	(013)	Monoclinic Ag <sub>2</sub> S
	40.4664	1.36095	2.2273	6.22	(031)	Monoclinic Ag <sub>2</sub> S
	44.0634	1.00959	2.0535	8.49	(103)	Monoclinic Ag <sub>2</sub> S
ZnS @ Ag <sub>2</sub> S 0.02 M	28.5314	3.62136	3.1260	2.26	(111)	Cub. ZnS
	47.3194	4.8451	1.9195	1.79	(220)	Cub. ZnS
	56.2294	3.83554	1.6346	2.35	(311)	Cub. ZnS
	34.2074	2.05125	2.6192	4.05	(121)	Monoclinic Ag <sub>2</sub> S
	36.5284	2.43698	2.4579	3.43	(112)	Monoclinic Ag <sub>2</sub> S
	40.2244	1.89186	2.2402	4.47	(031)	Monoclinic Ag <sub>2</sub> S
	43.0954	2.52866	2.0973	3.38	(122)	Monoclinic Ag <sub>2</sub> S

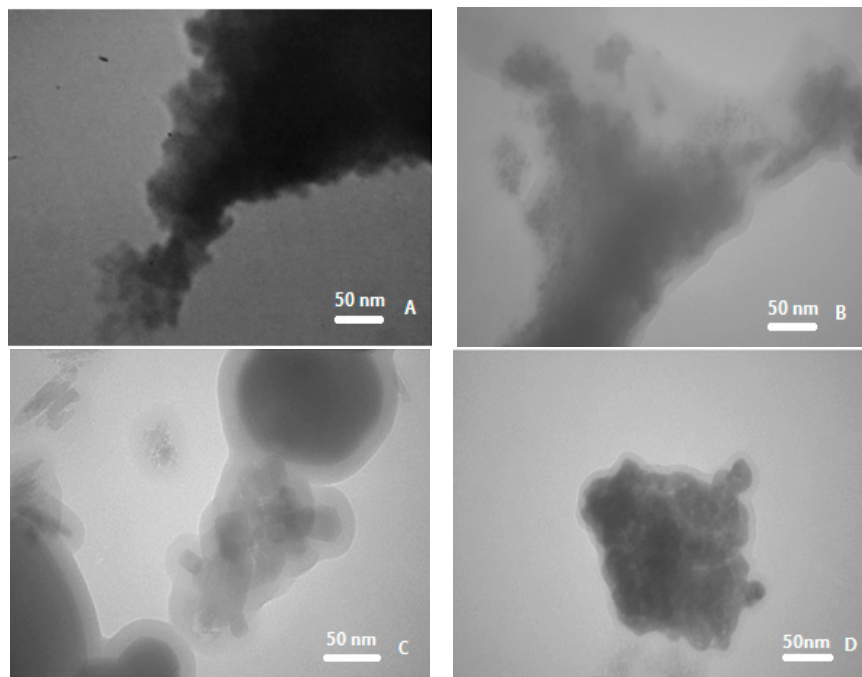
### 3.2 Transmission Electron Microscopy (TEM) Studies for ZnS NPs and ZnS@Ag<sub>2</sub>S NPs (Core/Shell)

Fig. 3 shows TEM images for ZnS NPs and ZnS@Ag<sub>2</sub>S NPs, with different concentrations of silver nitrate (0.005, 0.01, and 0.02 M), the image (A) shows clusters of ZnS NPs, lacking any silver sulfide layer [26]. However, when different concentrations of silver nitrate were added to ZnS NPs, a core and shell were observed around it, as shown in the images (B, C, and D). The image B (at 0.005 M) shows a combination of the core and shell, but it is less regular and homogeneous compared to image C (at 0.01 M), which shows a more regular and homogeneous arrangement of spherical particles. While, the image D (at 0.02 M) shows clusters of the core that are less homogeneous and surrounded by a regular shell, this is an agreement with [27]. Also, Fig. 4 shows the particle size distribution histograms, revealing that the homogeneity of the nanoparticles is clearly dependent on the silver nitrate concentration. ZnS NPs (A) exhibited a relatively narrow distribution within 10–20 nm, with the highest frequency in the 10–12 nm range. Upon incorporation of Ag<sub>2</sub>S as shell (0.005 M), (B) the distribution shifted toward larger sizes (10–35 nm) with a dominant frequency around 15–20 nm, indicating enhanced growth. At higher concentrations (0.01 M and 0.02 M, C and D), the distributions became comparatively narrower (10–22 nm and 6–22 nm, respectively), with the highest frequency centered near 16–18 nm and 12–14 nm. These results demonstrate a concentration-dependent modulation of particle size and frequency, confirming that Ag<sub>2</sub>S content significantly influences the nucleation–growth mechanism of the nanostructures.

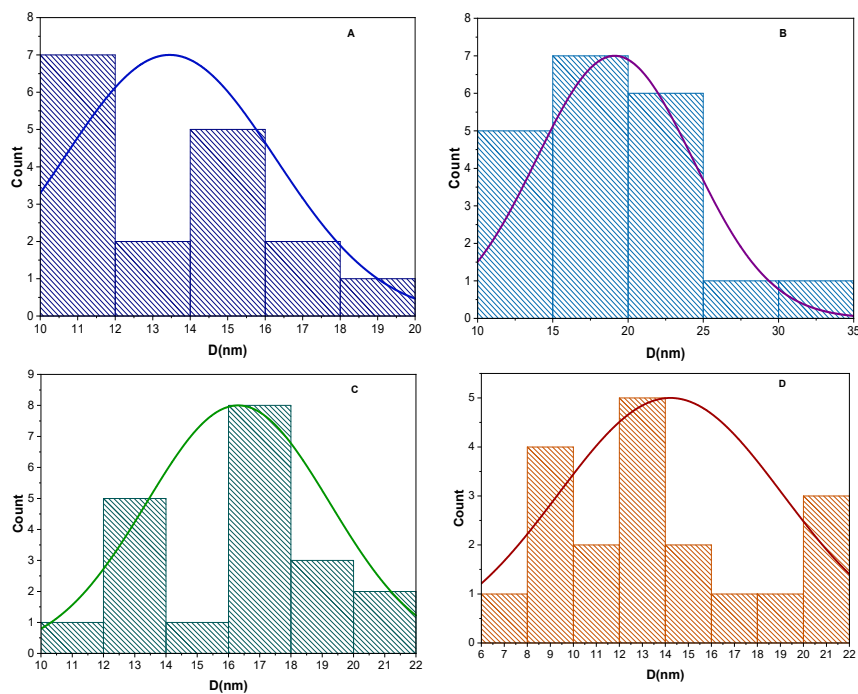
### 3.3 Energy Dispersive X-Ray (EDX) Analysis for ZnS NPs and ZnS@Ag<sub>2</sub>S NPs (Core/Shell)

In EDX analysis of ZnS NPs and ZnS@Ag<sub>2</sub>S NPs with AgNO<sub>3</sub> (0.005, 0.01, and 0.02 M), as shown in Fig. 5, the primary elements in ZnS NPs (A) were found to be (Zn) and (S) [28]. Also, carbon (C), and oxygen (O) were present which attributed to the components of the mint leaf extract used in the preparation, in addition to the apparent Na content originates from the overlap between Na K $\alpha$  and Zn L lines or may be indicate the actual presence of Na, this is in agreement with Senapati et al. [29]. While, in ZnS@Ag<sub>2</sub>S NPs (B–D) at different concentrations of silver nitrate, the results showed that zinc (Zn) and sulfur (S) remained balanced within the core/shell structure, in addition to the continued presence of oxygen and carbon in the composition, this indicates the ongoing influence of the organic extract [30]. As the concentration of silver nitrate increased from 0.005 to 0.02 M, a significant increase in the silver (Ag) content was observed, reaching 35.1% by weight and 12.6% by atomic ratio. These changes reflect the formation of silver sulfide

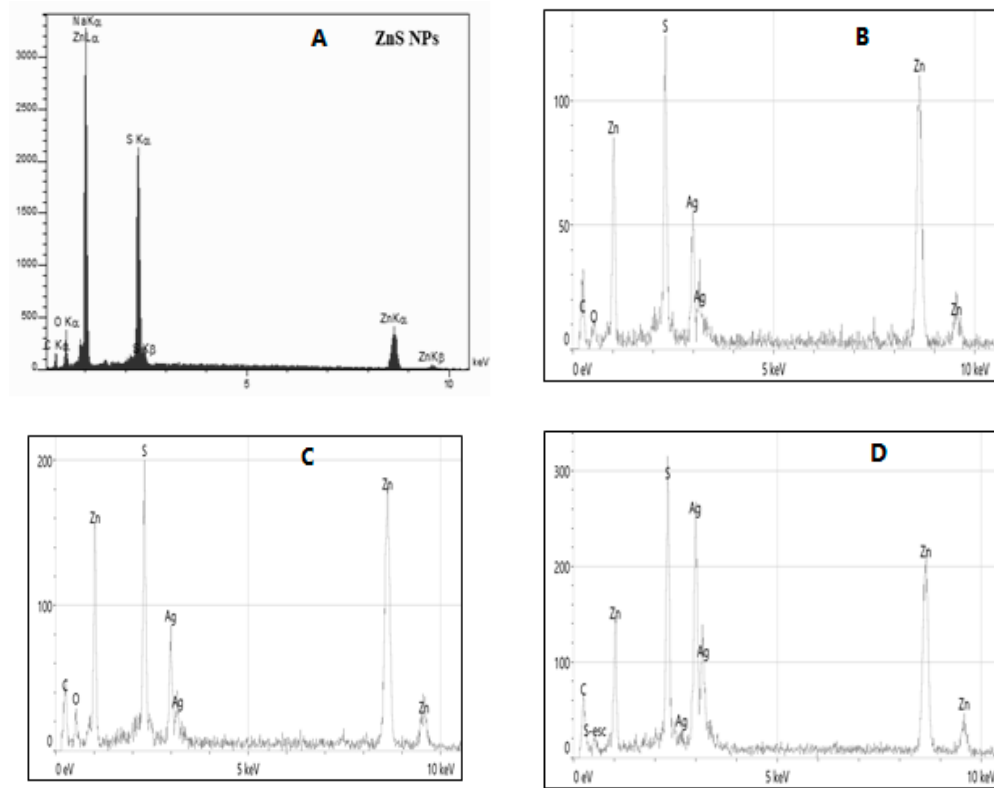
(Ag<sub>2</sub>S) around the zinc sulfide (ZnS) [31]. The weight and atomic ratios of the elements for ZnS and ZnS@Ag<sub>2</sub>S NPs are shown in Table 2.



**Figure 3:** TEM images for (A) ZnS NPs, (B) ZnS@Ag<sub>2</sub>S NPs (0.005 M), (C) ZnS@Ag<sub>2</sub>S NPs (0.01 M), (D) ZnS@Ag<sub>2</sub>S NPs (0.02 M).



**Figure 4:** Particle size distribution histograms for (A) ZnS NPs, (B) ZnS@Ag<sub>2</sub>S NPs (0.005 M), (C) ZnS@Ag<sub>2</sub>S NPs (0.01 M), (D) ZnS@Ag<sub>2</sub>S NPs (0.02 M).



**Figure 5:** EDX analysis for for (A) ZnS NPs, (B) ZnS@Ag<sub>2</sub>S NPs (0.005 M), (C) ZnS@Ag<sub>2</sub>S NPs (0.01 M), (D) ZnS@Ag<sub>2</sub>S NPs (0.02 M).

**Table 2:** The weight and atomic ratios of the elements for ZnS and ZnS@Ag<sub>2</sub>S NPs with different concentrations of AgNO<sub>3</sub>.

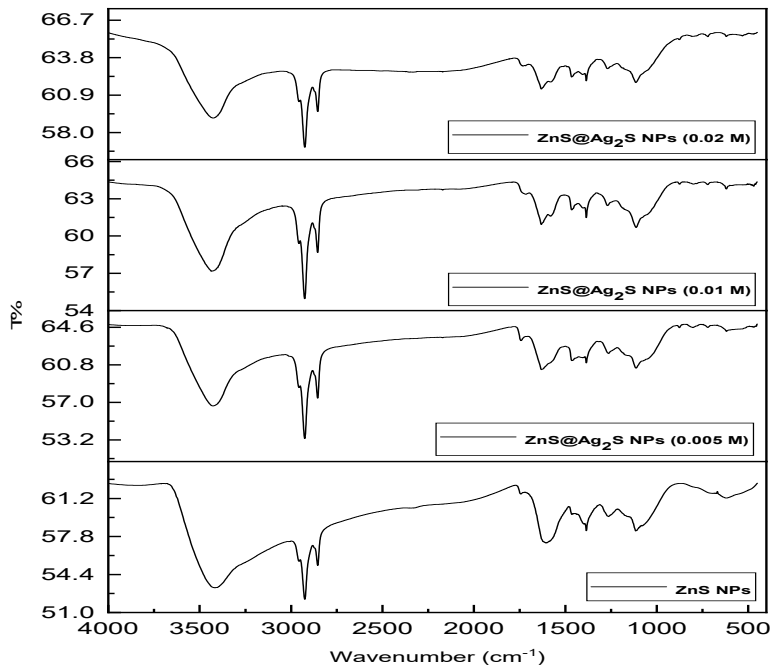
Samples	Elements	Weight %	Atomic %
ZnS NPs	C	15.40	35.51
	Na	16.28	19.61
	O	7.64	13.22
	S	13.54	11.69
	Zn	47.14	19.97
ZnS @ Ag <sub>2</sub> S 0.005 M	C	18.0	47.9
	O	5.1	10.2
	S	13.9	13.9
	Zn	48.1	23.5
	Ag	14.9	4.4
ZnS @ Ag <sub>2</sub> S 0.01 M	C	17.1	45.8
	O	6.5	13.2
	S	12.5	12.5
	Zn	48.7	24.0
	Ag	15.2	4.6
ZnS @ Ag <sub>2</sub> S 0.02 M	C	15.3	49.5
	S	13.7	16.6
	Zn	35.9	21.3
	Ag	35.1	12.6

### 3.4 Fourier Transform Infrared Analysis (FTIR) for ZnS NPs and ZnS@Ag<sub>2</sub>S NPs Core/Shell

The FTIR results of ZnS NPs and ZnS@Ag<sub>2</sub>S NPs, prepared using mint leaf extract at different concentrations of silver nitrate (0.005, 0.01, and 0.02 M) were analyzed, are shown in Fig. 6. The vibrational frequencies at the peaks 3413.94 cm<sup>-1</sup>, 3426.12 cm<sup>-1</sup>, 3435.98 cm<sup>-1</sup>, and 3426.26 cm<sup>-1</sup> for ZnS NPs and ZnS@Ag<sub>2</sub>S NPs, respectively indicate to stretching vibrations of the hydroxyl (O-H) groups present in menthol and other polyphenolic compounds from the mint extract, which acting as reducing and stabilizing agents for the nanoparticles, as well as contributing to controlling their growth and preventing agglomeration [32]. Vibrational frequencies at (2924.47 cm<sup>-1</sup>, 2924.97 cm<sup>-1</sup>, 2925.13 cm<sup>-1</sup> and 2924.70 cm<sup>-1</sup>), (2853.95 cm<sup>-1</sup>, 2854.28 cm<sup>-1</sup>, 2854.42 cm<sup>-1</sup>, and 2854.03 cm<sup>-1</sup>), for ZnS and ZnS@Ag<sub>2</sub>S NPs, respectively indicate to stretching vibrations of C-H bonds in hydrocarbon compounds, reflecting the chemical composition of organic compounds in the extract [33]. Also, the frequencies at (1384.73 cm<sup>-1</sup>, 1384.90 cm<sup>-1</sup>, 1384.94 cm<sup>-1</sup>, and 1384.93 cm<sup>-1</sup>) for ZnS and ZnS@Ag<sub>2</sub>S NPs, respectively and 1464.92, 1465.48, and 1465.82 cm<sup>-1</sup> for ZnS@Ag<sub>2</sub>S NPs indicate the bending vibrations of C-H groups in saturated hydrocarbons, particularly the methyl (CH<sub>3</sub>) and methylene (CH<sub>2</sub>) groups found in alkanes, the presence of these frequencies is indicative of the presence of organic compounds such as menthol and other terpenes found in mint leaf extract [34]. The frequencies at 1607.26 cm<sup>-1</sup>, 1630.99 cm<sup>-1</sup>, 1631.47 cm<sup>-1</sup> and 1631.18 cm<sup>-1</sup> for ZnS and ZnS@Ag<sub>2</sub>S NPs, respectively indicate C=C stretching vibrations in aromatic compounds such as phenols or menthol [17]. The frequencies at 1263.83 cm<sup>-1</sup>, 1263.27 cm<sup>-1</sup>, 1269.36 cm<sup>-1</sup>, and 1269.05 cm<sup>-1</sup> for ZnS and ZnS@Ag<sub>2</sub>S NPs, respectively refer to C-O stretching vibrations of alcohol and phenolic groups originating from menthol in the mint extract [35]. Also, the frequencies at 1114.75 cm<sup>-1</sup>, 1113.21 cm<sup>-1</sup>, 1112.53 cm<sup>-1</sup>, and 1114.12 cm<sup>-1</sup> for ZnS and ZnS@Ag<sub>2</sub>S NPs, respectively indicate to C-O or C-N bonds [36]. The frequencies at 622.62 cm<sup>-1</sup>, 619.03 cm<sup>-1</sup>, 619.55 cm<sup>-1</sup>, and 618.33 cm<sup>-1</sup> for ZnS and ZnS@Ag<sub>2</sub>S NPs, respectively indicate S-Zn bonds in zinc sulfide nanoparticles [37]. FTIR results also show significant changes in the spectrum of ZnS@Ag<sub>2</sub>S NPs compared to ZnS NPs, the transmittance (T%) increasing with increasing silver nitrate concentration, this suggests the formation of Ag<sub>2</sub>S as a coating around ZnS, furthermore, small peaks were observed between 450 and 900 cm<sup>-1</sup> in the spectrum of ZnS@Ag<sub>2</sub>S NPs, possibly indicating vibrations associated with S-Ag bonds [38]. FTIR bonds for ZnS and ZnS @Ag<sub>2</sub>S NPs synthesized by different concentrations of silver nitrate are listed in Table 3.

**Table 3:** FTIR bonds for ZnS and ZnS @Ag<sub>2</sub>S NPs.

Bonds	ZnS NPs	ZnS@Ag <sub>2</sub> S 0.005 M	ZnS@Ag <sub>2</sub> S 0.01 M	ZnS@Ag <sub>2</sub> S 0.02 M
O-H stretching vibrations	3413.94	3426.12	3435.98	3426.26
C-H stretching vibrations	2924.47 2853.95	2924.97 2854.28	2925.13 2854.42	2924.70 2854.03
C-H bending vibrations	1384.73	1384.90 1464.92	1384.94 1465.48	1384.93 1465.82
C=C stretching vibrations	1607.26	1630.99	1631.47	1631.18
C-O stretching vibrations	1263.83 1114.75	1263.27 1113.21	1269.36 1112.53	1269.05 1114.12
Zn-S bond	622.62	619.03	619.55	618.33

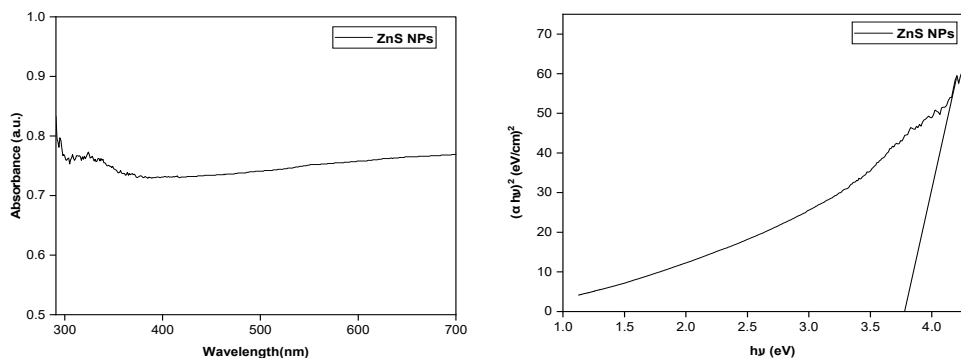


**Figure 6:** FTIR results of ZnS NPs and ZnS@Ag<sub>2</sub>S NPs with different concentrations of AgNO<sub>3</sub>.

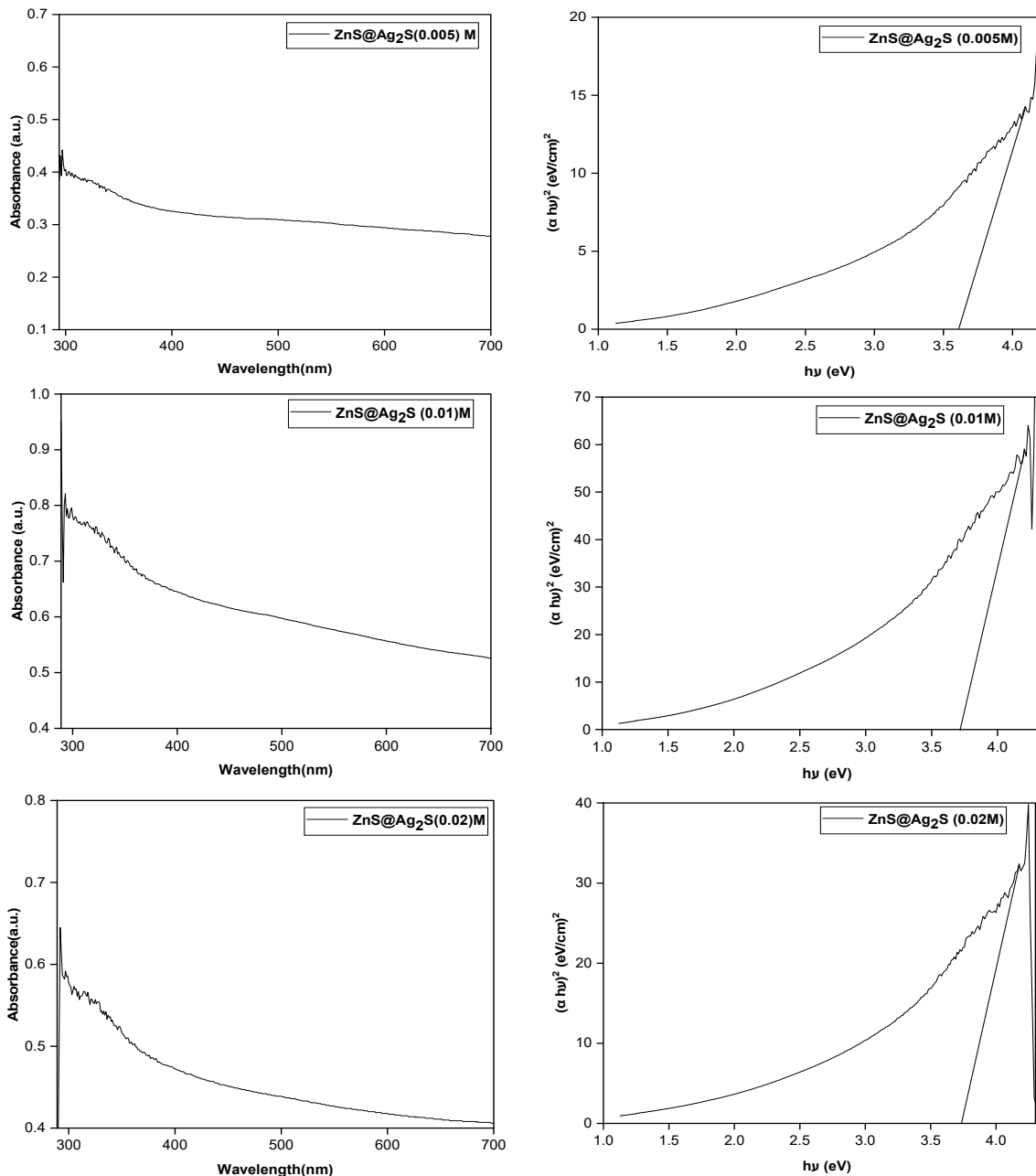
### 3.5 UV-Visible Spectra for ZnS NPs and ZnS@Ag<sub>2</sub>S NPs Core/Shell

The optical absorption spectra and Tauc plot analysis of ZnS NPs and ZnS@Ag<sub>2</sub>S NPs synthesized with different AgNO<sub>3</sub> concentrations (0.005, 0.01, and 0.02 M), as shown in Fig. 7, demonstrate a pronounced absorbance in the ultraviolet region [39]. The estimated optical band gap energies were found to be higher than that of bulk ZnS, which can be attributed to the quantum confinement effect arising from the nanoscale dimensions of the particles [40]. The band gap values were calculated to be 3.77, 3.61, 3.72, and 3.74 eV for ZnS NPs and ZnS@Ag<sub>2</sub>S NPs with AgNO<sub>3</sub> of 0.005, 0.01, and 0.02 M, respectively [41], using the Tauc relation (Eq. (2)) [42,43]. Furthermore, a slight reduction in the band gap was observed after coating ZnS NPs with Ag<sub>2</sub>S NPs, which can be ascribed to the formation of interfacial energy levels and electronic coupling between ZnS and Ag<sub>2</sub>S [44].

$$(\alpha h\nu)^r = B(h\nu - E_g) \quad (2)$$



**Figure 7:** Cont.



**Figure 7:** The optical absorption and Tauc plot analysis for ZnS NPs and ZnS@Ag<sub>2</sub>S NPs with AgNO<sub>3</sub> (0.005, 0.01, and 0.02 M).

#### 4 Conclusion

In this study, ZnS NPs and ZnS@Ag<sub>2</sub>S NPs were prepared using a green and environmentally friendly method that utilized peppermint leaf extract as both a reducing and coating agent. (XRD) results confirmed the successful formation of both ZnS and Ag<sub>2</sub>S phases, with an improvement in crystallinity as the silver nitrate concentration increased, indicating the controlled growth of the Ag<sub>2</sub>S layer around the ZnS core. Furthermore, the results showed an increase in ZnS crystal size after shell formation, while a gradual decrease in Ag<sub>2</sub>S crystal size was observed with increasing silver nitrate concentration. This can be attributed to an increase in the number of crystallization centers and a restriction of crystal growth at higher concentrations.

(TEM) images revealed a clear core-shell structure, with the Ag<sub>2</sub>S layer becoming more uniform and homogeneous at the silver nitrate concentration (0.01 M). EDX analysis confirmed a gradual increase in silver content with increasing concentration, indicating efficient and uniform encapsulation of ZnS particles within the Ag<sub>2</sub>S layer. FTIR revealed Zn–S and S–Ag bonds, along with characteristic vibrations of organic compounds present in the mint leaf extract, confirming the extract's dual role in reducing and surface stabilizing the nanoparticles. As for the ultraviolet-visible measurements, they showed a marked improvement in absorption behavior, with the absorption range expanding towards short wavelengths as the concentration of silver nitrate increased. This indicates an improvement in the ability of the composite nanoparticles to absorb radiation in the ultraviolet.

The improved optical absorption and the formation of a core-shell structure make these materials promising for various applications, such as photocatalysis, photonics, environmental applications, and antimicrobial applications. This study also confirms that using plant extracts is not only an environmentally friendly alternative to traditional chemical methods but also provides effective control over the structural and functional properties of nanoparticles.

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**Ethics Approval:** Not applicable.

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