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Preparation and characterization of the nanoparticles of pure zinc sulfide (ZnS NPs) and doped with silver (ZnS:Ag NPs) by green method using ascorbic acid

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Pure zinc sulfide nanoparticles and doped with silver (0.5,1,1.5,2.5, and 3.5) % wt. were prepared by green method. The structural properties were studied using X-ray diffraction technology(XRD). The diffraction patterns showed the particles were crystalline and had a zinc-blend structure with different average grain size. The surface topography was investigated by Scanning Electron Microscope (FE-SEM), it was found the shape is spherical and had different nanosized. Chemical purity was studied using Energy Dispersive X-ray Spectroscopy(EDX), the results showed the appearance of basic elements (Zn, S) and silver. The results of Fourier Transform Infrared Spectroscopy(FTIR) showed functional groups belonging to ascorbic acid, zinc, and sulfur. The topography and surface roughness were studied using an Atomic Force Microscope, it was found the particles have spherical shapes, roughness values, and various average grain sizes. The optical properties were studied using ultraviolet -visible light spectroscopy (UV-Vis), where the absorption spectrum showed strong distortions towards the ultraviolet region and a large value of optical energy gap compared with raw material.

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Keywords: Zinc sulfide nanoparticle, Silver, Green method, Ascorbic acid

1. Introduction

Zinc sulfide is considered one of the promising materials that belong to the second and fifth groups of the periodic table, which exists mainly in two structures, namely zinc blend and wurtzite, with direct energy gaps of 3.54 and 3.91 eV, respectively. [1] Zinc sulfide nanoparticles have unique properties that differ from their raw material counterparts due to their surface-to-volume ratio. (ZnS) NPs can be prepared using several physical and chemical techniques, but some of them have disadvantages [2]. Therefore, using green methods is considered one of the environmentally friendly, simple and inexpensive methods [3]. ZnS NPs have found applications in many fields, including, bioimaging [4, 5], skin regeneration [6], dye degradation [7, 8], catalyst [9, 10], growth of seed and plant [11, 12] , electronic devices [13, 14], sensing and optoelectronic fields[1] . The incorporation of transition metal ions into the ZnS nanoparticle lattice can significantly modify the material's characteristics, making them attractive for a variety of applications. the literature is replete with reports on the synthesis and characterization of transition metal-doped ZnS nanoparticles, with Mn, Co, Ni, and Fe being some of the most commonly studied dopants [15-18] . In addition to transition metal ions, rare earth metal ions have also been extensively used to dope semiconductor materials like ZnS and ZnO nanoparticles [19, 20]. The ionic radius of Ag+ is around 0.94 Å, while the ionic radius of Zn2+ is 0.74 Å. This relatively small difference in ionic radii allows the Ag+ ions to substitute Zn2+ ions in the ZnS crystal structure without significantly distorting the overall lattice [21].

This study aims to prepare zinc sulfide nanoparticles doped with silver in the green method and with the help of microwaves, and to study some of their physical properties.

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2. Preparation method and materials

2.1. Preparation of ZnS NPs

1- This work was done in a manner [22] with changes. sodium sulfide particles Na2S with (0.1M) and dissolved in (50ml) deionized water(DW) were added to aqueous zinc nitrate particles Zn(NO3)2.6H2O with (0.1M) and dissolved in(50ml) deionized water and left under magnetic stirring

for 15 minutes. It was observed that the solution turned white.

2- The solution was placed in the microwave at 550 watts for one minute.

3- After that, 20 ml of ascorbic acid with concentration (0.5 M), dissolved in (50 ml) DW, is added to the solution with continuous stirring for 30 minutes.

4- Then the solution is placed in the microwave at the same power for one minute, after which the solution is returned under continuous stirring for 30 minutes.

5- Precipitates obtained are centrifuged with 4,000 rpm for 10 mints, and washed twice by DW and once by ethanol (99.9).

6- After collecting the formed Precipitate, it is left to dry for a night, and after drying it becomes yellow in color and is ready for characterization.

2.2. Preparation of ZnS: Ag NPs

1- The concentrated of Na2S (0.1 M) dissolved in 50 ml of DW is added to the (0.1 M) of Zn) NO3)2.6H2O dissolved in 50 ml of DW, with continuous stirring for 15 minutes. After that, the solution is placed in microwave with (550 watts) for one minute, and then it is placed under continuous stirring for 30 minutes.

2- The precipitate formed was separated using centrifugation with (4,000 rpm for 10 mints), then washed twice with DW for 15 minutes.

3- The resulting precipitate is collected and diluted with 50 ml of DW, then silver nitrate AgNO3 dissolved in 50 ml of DW is added to it in proportions (0.5, 1, 1.5, 2.5, and 3.5) % wt. (0.00502, 0.00101, 0.00152, 0.00256, 0.00362) M, respectively. Which was calculated according to the following equation [23]:

$$\%\text{dopants} = M\ (\text{AgNO}_3)\ molarity\ /M\ (\text{AgNO}_3) + M\ \text{Zn(NO}_3)_2.6H2\text{O} \quad \ldots (1)$$

4- After that, 20 ml of ascorbic acid is added with continuous stirring for 15 minutes, then the mixture is placed in the microwave for a minute, and finally the mixture is placed under the magnetic stirrer for 30 minutes.

5- The precipitate is separated, washed, and then dried according to the paragraph (2.1) to be ready for characterization.

3. Results and discussion

3.1. The Measurement of XRD analysis

The XRD pattern shown in Fig 1 indicates the crystalline nature of the prepared ZnS and ZnS:Ag nanoparticles. The most prominent feature in the XRD pattern is the peak at $2\theta = 28.834°$, which is assigned to the (111) reflection of the cubic zinc blende structure of ZnS, based on the JCPDS reference (No. 5-566). Two other peaks are observed at $2\theta = 47.976°$ and 56.810°, corresponding to the (220) and (311) reflections respectively, further confirming the cubic zinc blende crystal structure. The presence of these characteristic XRD peaks provides evidence that the synthesized ZnS and ZnS:Ag nanoparticles have successfully adopted the expected cubic zinc blende crystalline phase. The well-defined XRD pattern suggests the prepared nanoparticles have good crystallinity, without significant amorphous content [24]. The structure of ZnS remained virtually unchanged by the incorporation of the dopants. The doping has affected both the Full Width at Half Maximum (FWHM) intensity, and the peak position of XRD patterns by which that the peaks position shifts toward the longer 2Θ side as shown in Table 1. It was also observed at doping rates (0.5 %,1% ,1.5 %) that no diffraction peaks appeared for silver, this may be due to the low concentration used in the study. Because of the close ionic radii of both silver and zinc, it is expected that the doping of the crystal lattice of zinc sulfide is interchangeable between silver and zinc, as well as in order to maintain the electrical equivalence of the crystal lattice. Table 1 shows the particle size, which was calculated depending on Scherer's equation $D = K \lambda / \beta \ \mathrm{Cos}\ \Theta$ [25, 26]. The results appear there is an increase in the value of average grain size of ZnS:Ag NPs compared to pure ZnS NPs ,the reason for this is due to the reactions that occur between the additives and nanoparticles.

Table 1. The structural parameters of ZnS and ZnS NPs.

Sample	2θ (Deg.)	FWHM (Deg.)	d_{hkl} Exp.(Å)	G.S (nm)	hkl	Phase
Pure ZnS	28.834	2.9447	3.0938	2.79	(111)	Cub. ZnS
	47.976	3.0920	1.8948	2.81	(220)	Cub. ZnS
	56.810	2.9448	1.6193	3.07	(311)	Cub. ZnS
				Av.= 2.89		
0.5 % (Ag)	28.393	2.4295	3.1409	3.37	(111)	Cub. ZnS
	47.387	2.2822	1.9169	3.80	(220)	Cub. ZnS
	56.295	2.4295	1.6329	3.71	(311)	Cub. ZnS
				Av.= 3.62		
1 % (Ag)	28.461	2.6504	3.1336	3.09	(111)	Cub. ZnS
	47.455	2.6503	1.9143	3.28	(220)	Cub. ZnS
	56.363	2.4295	1.6311	3.71	(311)	Cub. ZnS
				Av.= 3.36		
1.5 % (Ag)	28.466	2.6940	3.1330	3.04	(111)	Cub. ZnS
	47.534	2.5767	1.9113	3.37	(220)	Cub. ZnS
	56.295	2.5030	1.6329	3.60	(311)	Cub. ZnS
				Av.= 3.33		
	28.614	2.7040	3.1172	3.03	(111)	Cub. ZnS
2.5 % (Ag)	38.184	0.8098	2.3550	10.39	(111)	Cub. Ag
	47.681	2.7976	1.9058	3.11	(220)	Cub. ZnS
	56.589	2.5031	1.6251	3.61	(311)	Cub. ZnS
				Av.= 5.03		
3.5 % (Ag)	28.593	2.7300	3.1194	3.00	(111)	Cub. ZnS
	38.384	0.7361	2.3432	11.43	(111)	Cub. Ag
	44.642	0.6626	2.0282	12.97	(200)	Cub. Ag
	47.734	2.5031	1.9038	3.47	(220)	Cub. ZnS
	56.495	2.5030	1.6276	3.60	(311)	Cub. ZnS
				Av.= 6.89		

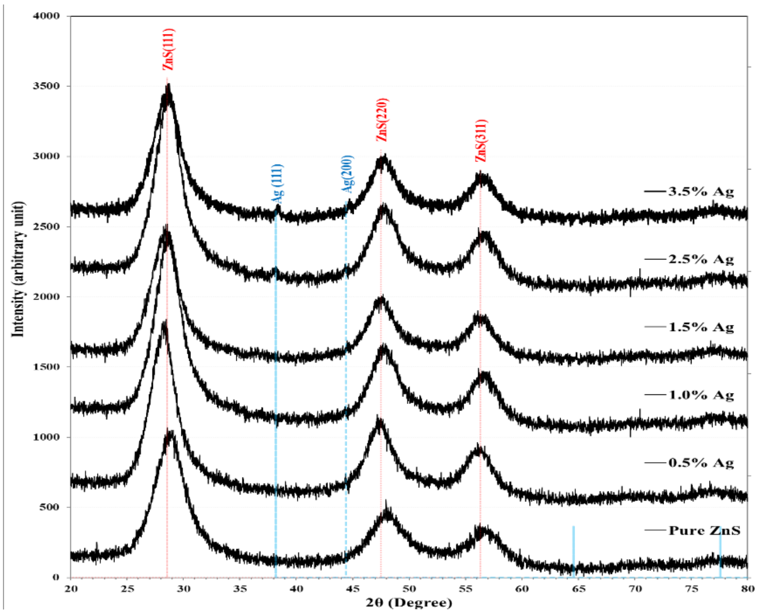

Fig. 1. Patterns of XRD for ZnS and ZnS:Ag NPs.

3.2. Measurement of (FE-SEM)

The surface topography and size of pure zinc sulfide nanoparticles and doping with silver particles were characterized using FE-SEM, as shown in Fig 2. Images (a, b, c, d, e, and f) show that the shape spherical [27] with an average particle size of about (26.85, 31.93 ,37.33, 37.02, 30.97, 33.34) nm, for pure ZnS and after doped with (0.5,1,1.5,2.5, and 3.5) % wt of Ag.

3.3. Result of (EDX)

The chemical purity and elemental percentage of ZnS and ZnS: Ag at doping ratios (0.5,1,1.5 ,2.5,and 3.5) % which was prepared by green method using ascorbic acid was tested by EDX spectrum as shown in Fig 3, EDX results shown in Table 2, it refers to the two basic elements (S and Zn) , in addition to carbon and oxygen, which are due to the natural material used for preparation, as well as percentages of silver, except for the two percentages (0.5 and 1) % in which no weight percentages of silver appeared. Perhaps the reason for this is due to the small weight percentages used.

3.4. FTIR measurements

The FT-IR spectra for as-synthesized samples are shown in Fig 4. A broad peak at 3442 cm-1 is due to the stretching vibration of OH [28], 2372cm-1 and 2320 cm-1 peaks due to C-H stretching vibration, the peaks at 1870 cm-1, 1683 cm-1 , 1651 cm-1 due to C=O stretching vibration [29], 1560 cm-1 ,1396 cm-1 due to asymmetric nitro bond, while the peak at 1342 cm-1 due to symmetric nitro bond (C-H bend)[30]. These peaks confirm the essential role played by the natural organic substance (ascorbic acid) as a reducing and covering agent for ZnS and ZnS doped with Ag. The FT-IR spectra show characteristic vibration peaks for ZnS in the range of 400-650 cm-1, there is an increase in the absorption range for values greater than 650 cm-1 as the impregnation rate increases, and this indicates the connection between silver and ZnS [31].

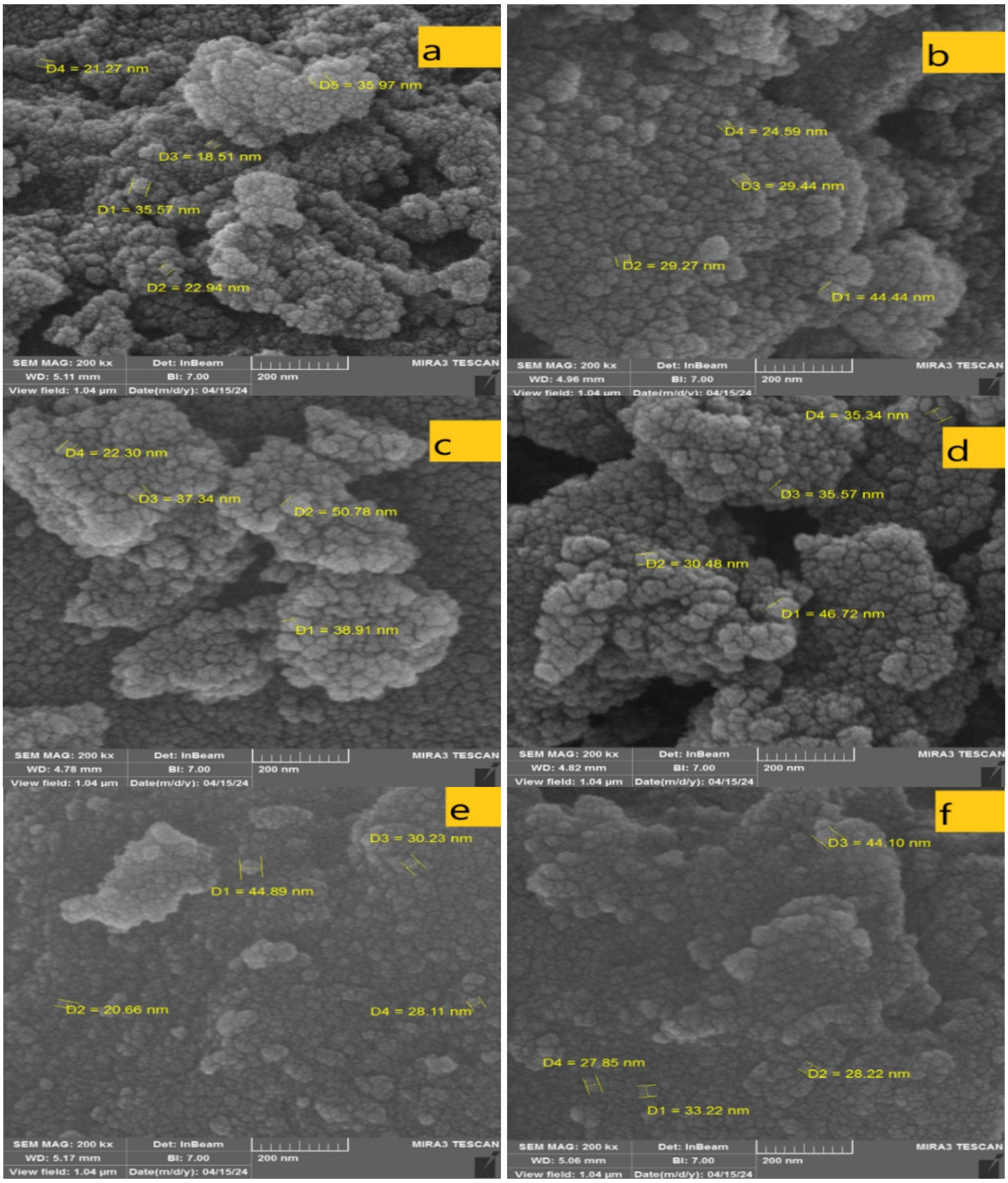

Fig. 2. Shows electron microscope images of spherical shapes and different diameters of particles.

Table 2. The chemical purity and elemental percentage of ZnS and ZnS: Ag.

Samples	Elements	Weight%	Atomic%
undoped	C	11.75	26.71
	O	11.73	20.02
	S	49.15	41.85
	Zn	27.37	11.43
0.5 %	C	10.38	24.03
	O	11.12	19.33
	S	52.68	45.67
	Zn	25.82	10.98
1%	C	10.03	22.92
	O	13.68	23.47
	S	49.47	42.35
	Zn	26.82	11.26
1.5%	C	8.68	23.58
	O	3.00	6.12
	S	52.31	53.23
	Zn	31.43	15.69
	Ag	4.59	1.39
2.5%	C	21.66	45.74
	O	5.54	8.78
	S	45.04	35.63
	Zn	21.76	8.44
	Ag	6.01	1.41
3.5%	C	10.63	28.17
	O	2.81	5.60
	S	50.69	50.31
	Zn	27.87	13.57
	Ag	8.00	2.36

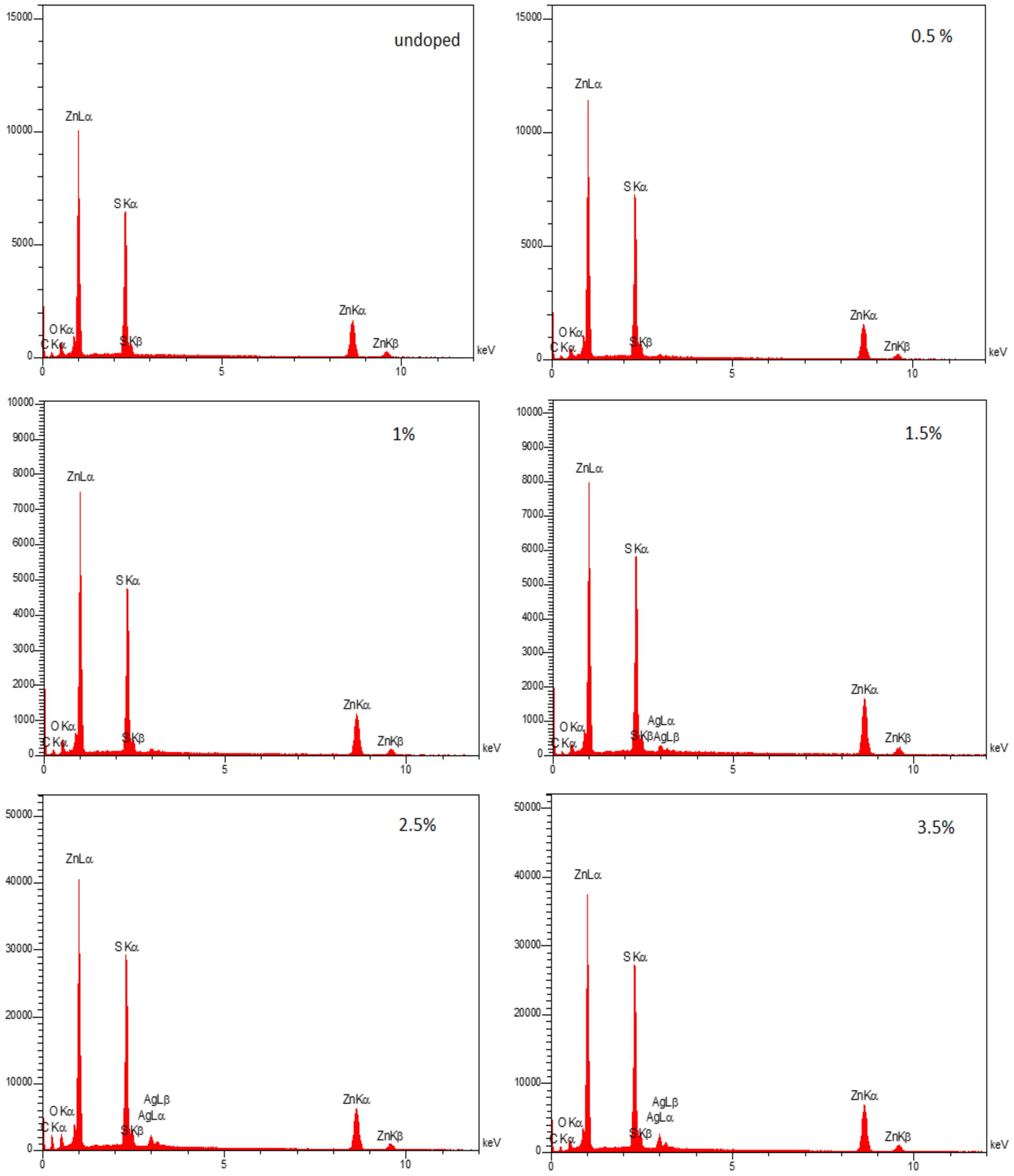

Fig. 3. Shows the chemical purity of the prepared samples.

3.5. AFM analysis

The roughness and topographic of NPs have been seen by atomic force microscopy to provide an extensive surface inspection of the microstructural arrays, the Fig 5 shows that all samples have spherical shapes, the average diameter of the granules and the roughness as shown in Table3 where changes in surface height were observed at the nanoscale, which gives the surface a rough topography, but with varying values.

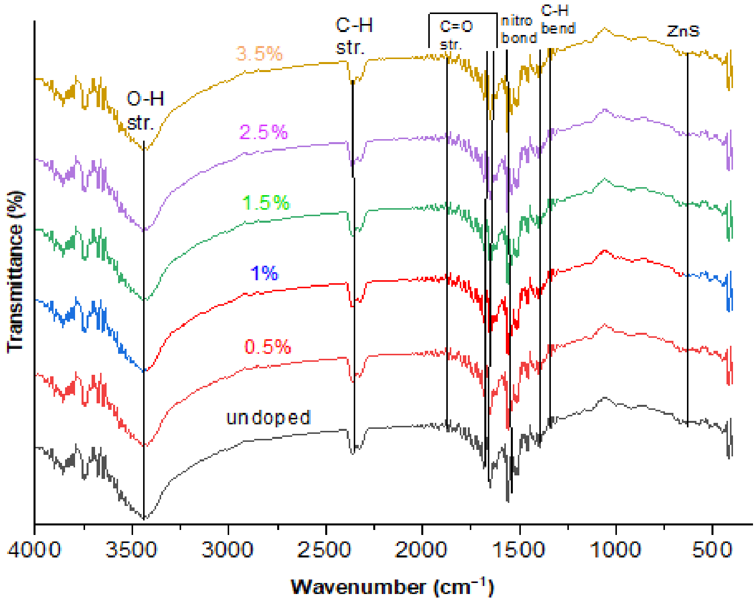

Fig. 4. Shows the frequency vibrations of functional groups and zinc sulfide.

Table 3. Shows the particle diameter rate and surface roughness rate.

Sample	Average dimeter of the particles in (nm)	The roughness in (nm)
Pure ZnS NPs	83	19
ZnS doped with 0.5 % Ag	86	22
ZnS doped with 1% Ag	73	20
ZnS doped with 1.5 % Ag	73	24
ZnS doped with 2.5 % Ag	74	16
ZnS doped with 3.5 % Ag	70	20

3.6. UV-Vis analysis

The optical properties of ZnS and ZnS :Ag NPs were studied using UV-visible light spectroscopy, as shown in Fig 6. It was noted that the absorption spectrum appeared in the ultraviolet region compared to the raw material, and this indicates that the size of the material has become on the nano scale [29] . When the rays fall from the source, whether they are ultraviolet or visible light, they will be absorbed by the valence electrons. If the energy of these rays is sufficient for the transfer of electrons, then it is possible to calculate the optical energy gap (Eg) from the following equation Eg = h C/λ[32, 33] . The energy band gap of ZnS:Ag NPs which found bigger than of pure ZnS NPs as shown Table 4 , When impurities or foreign elements are added to a pure substance, the size of the substance becomes limited at the atomic level. This quantum effect leads to an increase in the optical energy gap, as the energy of the trapped electrons increases. Or perhaps this is due to the formation of new levels in the energy gap, and the presence of these new levels leads to an increase in the apparent optical gap[34].

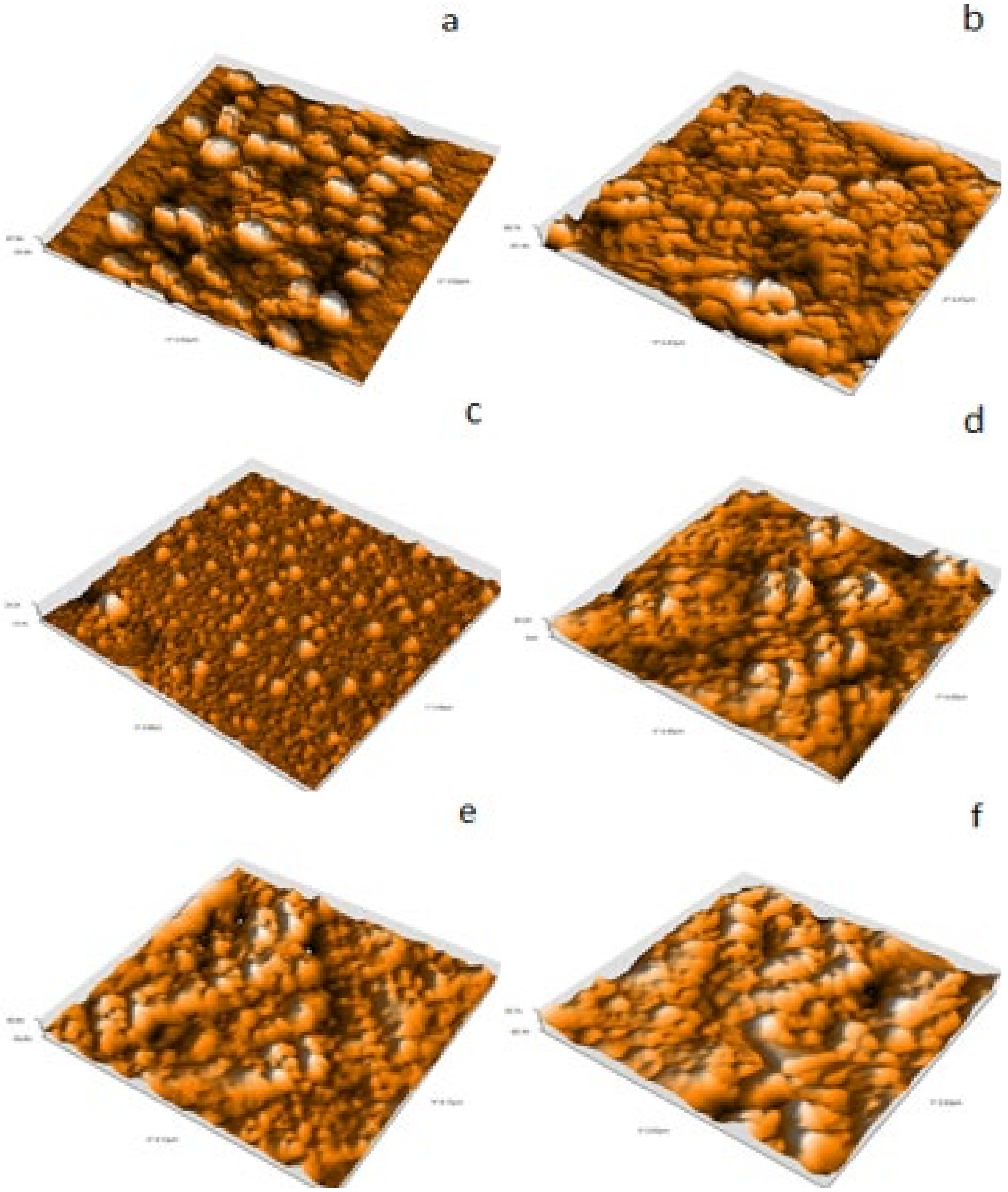

Fig. 5. Atomic force microscope images of the prepared samples (a, b, c, d, e, and f) for pure ZnS and doped with (0.5, 1, 1.5, 2.5, and 3.5) %Ag, respectively.

Table 4. Shows the optical energy gap and the wavelengths at which the highest absorption occurs.

Sample	Energy gab (eV)	Wavelength in (nm)
Un doped ZnS	3.97	312
0.5%	5.9	210
1%	5.9	210
1.5%	5.82	212
2.5%	5.87	211
3.5%	5.96	208

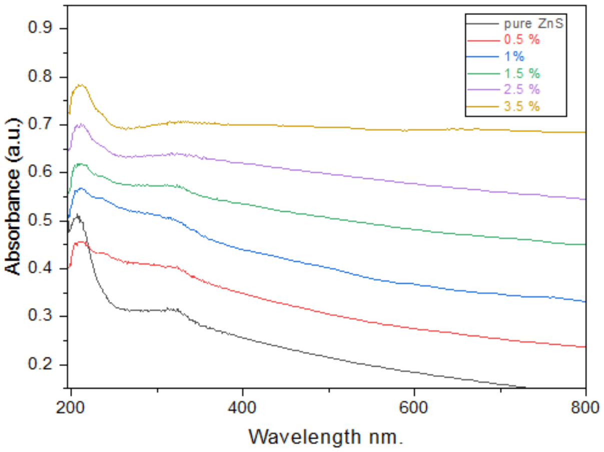

Fig. 6. It shows the highest absorbance for pure and grafted particles at different concentrations.

4. Conclusion

We concluded from our study that the method used in the study was easy, inexpensive and not harmful because of its use a coverage and reduction factor that is considered one of the natural materials, which is ascorbic acid. Through tests carried out to study the compositional, morphological and optical properties, we found that the particles were crystalline, with a zinc-blend composition, and of different nanosized after grafting, and that the ascorbic acid played the role of a covering agent and a reducing agent, leading to the particles forming in spherical shapes and with different surface roughness values. The formation of nanoscale particles led to an increase in the optical energy gap compared to the raw material. As a result, the addition of silver led to a change in some physical properties of pure zinc sulfide.

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