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MICROWAVE ASSISTED SYNTHESIS OF ZnS & ZnS-Ag NANOPARTICLES AND ITS ANTIBACTERIAL ACTIVITY

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ABSTRACT

ZnS, ZnS-Ag nanoparticles were successfully synthesized by Microwave assisted irradiation method using glucose, both as capping agent and as stabilizer. The resulted nanoparticles are characterized using X-ray diffraction (XRD) and UV-vis optical absorption techniques. XRD characterization of nanoparticles verified the crystalline form. The average size of the nanocrystallites was measured by Debye-Scherrer formula. The mean particle size of the ZnS nanoparticles was 3 nm and for ZnS-Ag nanoparticle was 2.4 nm.The optical characterization of these nanoparticles by UV-vis absorption spectra and the optical bandgap were 3.85 and 3.95 eV respectively. The coating of the nanoparticles by glucose was confirmed by the FTIR spectroscopy.The MIC tests demonstrated that 37.5 µg/ml and 75µg/ml of ZnS NPs and ZnS- Ag respectively were the best antibacterial activity against both *Pseudomonas aeruginosa* and *Staphylococcus aureus.*

KEYWORDS: Microwave, Glucose, ZnS, ZnS-Ag, XRD, UV, FTIR, Antibacterial effect.

INTRODUCTION

Nanotechnology is the tool for production, design, characterization and applications of nanoparticle material, it generally deals with the structures sized between 1-100 nanometers in at least one dimension [1]. Nanoparticles of semiconductors that have many application such as uses in light emitting diode, phosphors in lighting, displays, solar cell, X-ray sensors and window material, photo catalyst and electrochemical cell, the Zinc Sulfide (ZnS) is one of this family[2]. II-VI class inorganic semiconductor nanomaterials like CdS, ZnS, CdSe emerged as important materials for the applications in optoelectronics devices. ZnS is extensively studied becauseit has numerous applications to its credit [3,4]. Regrding to the important of phosphor at photoluminescence (PL), cathode luminescence (CL) and electroluminescence (EL) devices because of ithas avery good chemical stability in comparison with otherchalcogenides [2].Silver NPs are one of the most important materials becauseit has unique properties such as size, shape, optical, electrical, and magnetic properties. Which can be incorporated into antimicrobial applications, biosensor materials, composite fibers, cryogenic super conducting materials, cosmetic products, and electronic components catalysts in chemical reactions, electrical batteries and in the coating the solar energy cells. Several physical and chemical methods have been used for synthesizing and stabilizing silver NPs [5-7]. Glucose which is a simple monosaccharide found in plants with five hydroxyl groups are arranged in a specific way along its six carbon backbone. Glucose as a "Green" reagent has been selected as a capping agent because it has unique Properties such as abundant, natural, renewable and biodegradable. Since it is biodegradable, it may also help in reducing cytotoxicity problem of nonmaterial's [3,8].Microwave irradiation methods is one of the various irradiation method for preparing nanoparticles. Microwave irradiation has attracted chemists' attention, although the exact nature of the interaction between reactants and microwaves during the preparation of materials is not known understood. Different from normal heating, where the heating energy is transferred from outside to inside, microwave irradiation induces interaction of the dipole moment or molecular ionic aggregates with alternating electronic and magnetic fields causing molecular-level heating, which leads to a homogenous and quick thermal reaction. Compared with conventional methods[9,10].the current work amied to prepare of ZnS, ZnS- Ag nanoparticles in a simple ,eco-friendly and economical method by using microwave and using glucose as a capping agent, to stabilized nanoparticles[14]. And to achieve theiractivity against multidrug resistance pathogenic bacteriaStrains. Nanoparticles of ZnS showed antimicrobial activity against both Gram positive and Gram negative strains except *Shigella sonnei*. The anticancer drug imatinib was inhibitory for only Gram positive organisms, *Bacillus subtilis* and *Staphyloccus aureus*. Synergism between imatinib and ZnS nanoparticles was distinctly observed in all the Gram positive strains. The main advantage of ZnS nanoparticles of diameter 29 nm.

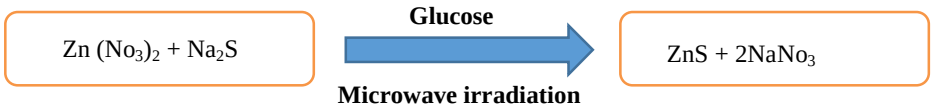
The Experimental Part

$Zn(NO_3)_2$ was used as Zinc source and Na_2S was used Sulphur source. $Zn(NO_3)_2$, Na_2S, $AgNO_3$, and glucose are obtained from Merck Specialities Private Ltd. and Qualigens fine chemicals respectively. These are of high purity and used without any future purification. The

samples were prepared by Microwave assisted synthesis of nanoparticles.

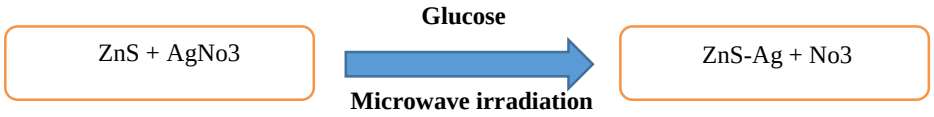
Synthesisof ZnS

Zinc nitrate Zn $(NO_3)_2$ dissolves in (50 ml) distal water , sodium sulphide Na_2S dissolves in (50ml) distal water , In Zn $(NO^3)_2$ solution, Na_2S solution is added drop wise with continuous stirring. A white coloured solution is Formed which is further shaken on a magnetic stirrer for (15 min). Now the product put in Microwave for a (1min), then takes it out and place in magnatic stirrer and the addition of dissolved glucose in (10ml) distal water drops into the mix with continuous stirrer for (30min). And put in Microwave for a (1min). Now, return the mix On magnetic stirrer for (30 min).Precipitates obtained are centrifuged with 4,000 rpm for 10mins. The final product is dried at 65C for 3 hours and then crushed to fine powder. The Synthesis process can be summarized by the chemical equation given below (1):



Synthesis of ZnS-Ag

Zinc nitrate Zn $(NO_3)_2$ dissolves in (50 ml) distal water , sodium sulphide (Na2S) dissolves in (50ml) distal water, In Zn $(NO_3)_2$ solution, Na_2S solution is added drop wise with continuous stirring. A white coloured solution is formed which is further shaken on a magnetic stirrer for (15 min). Now the product put in Microwave for a (1min), return the mix on magnetic stirrer (30min). Precipitates obtained are centrifuged with 4,000 rpm for 15 mints .The supernatant was collected and The volume is supplemented to (50ml) and place in magnetic stirrer and the addition of dissolved $AgNO_3$ in (50ml) distal water drops into the mix with continuous stirrer and addition of dissolved glucose in (10ml) distal water drops into the mix with continuous stirrer for (15min). And put in microwave for a (1min). Now, return the mix on magnetic stirrer for (30 min).Precipitates obtained are centrifuged with 4,000 rpm for 15 mints. The final product is dried at 65ºC for 3 hours and then crushed to fine powder. The Synthesis process can be summarized by the chemical equation given below (2):



Media

In order to keep the bacteria in their activity as in the body of the organism must be placed in a situation characterized by conditions similar to the original conditions that lived in and that the isolates used in this experiment were actived by brain heart broth and brain heart agar. And for MIC test Mueller Hinton broth/agar was used. It was prepared with a weight 15.2 gm of medium and dissolved in 400 ml of distilled water.

Determination of the antibacterial activity of the ZnS and ZnS: Ag nanoparticles

Minimum inhibitor concentration (MIC) method:

Three kinds of multi drug resistance bacteria were provided for this study from department of biotechnology –College of science/ Baghdad University, which were *Pseudomonas aeruginosa andStaphylococcus aureus*

This method is used to determine the levels of microbial resistance to a particular antimicrobial agent. The lowest concentration of antimicrobial agent preventing level of turbidity is considered to be the minimal / minimum inhibitory concentration of that particular agent. Thus MIC was performed to determine the concentration of biosynthesized nanoparticles showing growth inhibition of bacterial strains [15].

ZnS and ZnS: Ag NPs were added in Mueller Hinton Medium, respectively. Each bacteriumculture *S. aureus* and*Pseudomonas aeruginosa*was controlled at 10^5-10^6 CFU/mL and incubated at 37ºC .Toestablish the antimicrobial activity of ZnS,ZnS;Agnanoparticles on the bacterialgrowth, the minimum inhibitoryconcentration of nanoparticles shapes forthese bacteria were determined byoptical density of the bacterial culture solution containing different concentration of ZnS,ZnS;Ag NPs after 24h. All of the experiments (MIC) were triplicated, on three different days were inoculated in the shaking incubator.

RESULTS & DISCUSSION

Structure characterization of ZnS, ZnS-Ag nanoparticles:

X-Ray Diffraction (XRD) patterns of prepared ZnS, ZnS-Ag nanoparticles in figure (1) below demonstrates three broad peaks in the diffractrogram at around 28.7663, 48.1283, 56.6017 corresponds to (111), (220) and (311) planes of cubic ZnS ,respectively.

XRD pattern of ZnS-Ag nanobarticles has pointed and more intense peaks than the undoped ZnS nanobarticles, which indicates that the synthesized ZnS-Ag nanoballs were crystalline in nature. The spectra show various diffraction peaks at 2h values of 28.7194 , 47.8615 and

56.5496 corresponding to the diffraction planes (111), (220) and (311), respectively.

Our results agreed with N.SOLTANI, E. SAION, *et al*, and A. Rahdar, V. Arbabi, *et al*.[16][17].

The average crystallite size was calculated using DebyeScherer formula [16].

$D = K\lambda / \beta \cos \Theta$ …….. (1) , where D is the crystallite size, K is the geometric factor (0.9), λ is the X-ray wavelength (1.54A°), β is the full with at half maxima (FWHM) of the diffraction peak (in radian) and cos Θ is the diffraction angle[3][18].

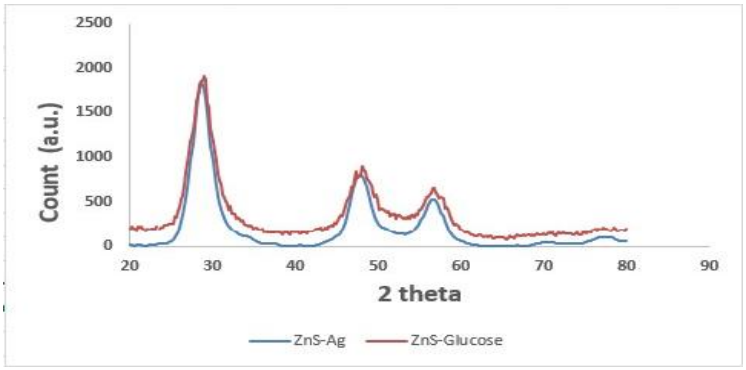


FIGURE 1: XRD of ZnS, ZnS-Ag nanoparticles with 2 theta

According to this formula the average crystallite sizes were 3nm and 2.85nm, respectively. As shown in table (1 (a & b)).

Optical characterization

From the Optical characterization, (UV-Visible) analysis determines the nanomaterials formation, and calculates the value of band gap energy which is known as the energy difference between the top of the valence band and the bottom of the conduction band. The values of the band gap of ZnS nanoparticles are calculated from eq. (2) listed in the table (1a) below is higher than that of the bulk value of ZnS (3.68eV), this agree with Senapati, U.S., Jha, D.K., Sarkar D. [3] this blue shift of the band gap takes place because of the quantum confinement effect, the band gap changes can be due to nanoparticle size change using the effective mass approximation (EMA) method, the effective mass model is commonly used to study the size dependence of optical properties of quantum dots (QD) system [19]. The optical absorption spectrum of Nanoparticles Zns and Zns-Ag is shown in Figure (2).

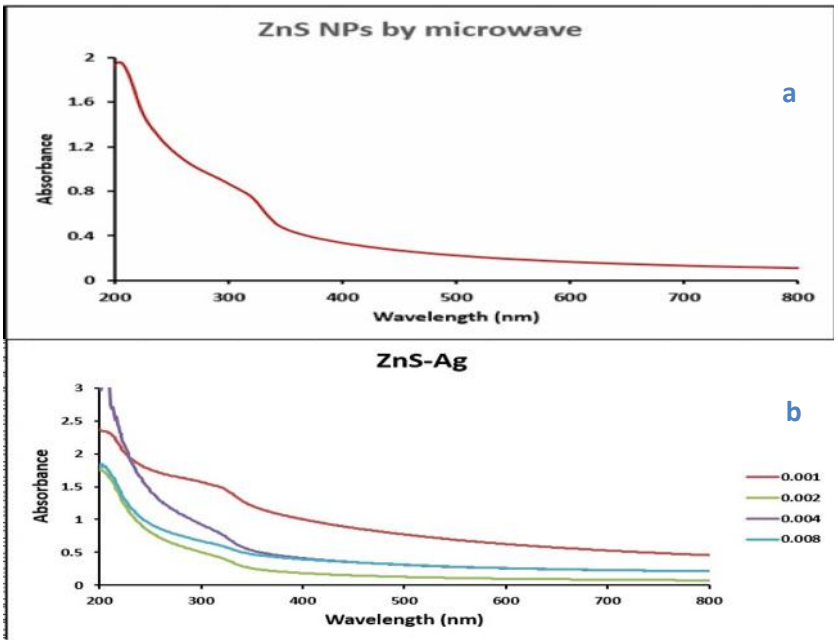


FIGURE 2: UV-Vis Absorption spectrum of (a: ZnS and b: ZnS-Ag) nanoparticles

The band gap of ZnS, ZnS-Ag Nanoparticles calculated from using the following equation: (E) =hc/λ…..(2) Were (E) is the band gap , (h) plank constant and equal,(c) light speed,(λ)wave length .

The band gap of ZnS-Ag in table (1b) observed that with the concentration of AgNo3doping increased the peak absorption wavelength (λ_p) increased the energy gap decreasing. The decreasing of energy gaps with doping can be attributed to the creation levels at the energy bands.

TABLE 1a: the band gap of ZnS, b: the band gap of ZnS-Ag (a) ZnS (b) ZnS-Ag

$Zn(NO_3)_2$ Na_2S Concentration (µ)	Wave Length (λ)	Optical band gap (E)(eV)	Particles size(nm) From XRD
0.1	292	4.25	3.06

AgNO3 Concentration(µ)	Wave Length(λ)	Optical band gap (E) (eV)	Particles size(nm) From XRD
0.001	304	4.08	-
0.002	308	4.03	2.85
0.004	309	4.02	-
0.008	325	3.82	-

This might be due to the fact that AgNO3forms new energy levels in the ZnS energy band. Due to quantum size effects the particle size decrease with decreasing the band gap energy, and with increasing the $AgNO_3$concentration, it shows that $AgNO_3$can be a suitable capping agent for ZnS, that controls the growth of ZnS nanoparticles It is to be pointed out that the size of ZnS estimated from the optical absorption study for sample with 0.002M of $AgNO_3$is comparable to this obtained from the XRD analysis.

Fourier Transform Infra-Red Spectroscopy (FTIR):FTIR measurements were carried out using infra-red spectrometer by employing KBr pellet technique. The powdered nanoparticles sample was prepared by centrifuging the synthesized ZnS-AgNPs solution at 13,000 rpmfor 15min. The solid residue layer which contains NPs was dried perfectly at 37° C overnight.

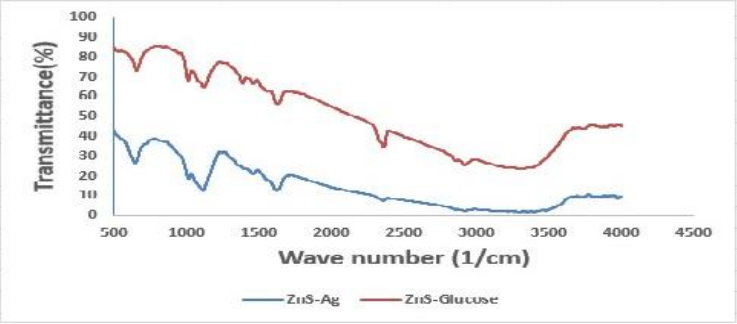


FIGURE 3: FTIR spectra of ZnS-Ag nanoparticles

Figure (3) shows the FTIR spectrum of the ZnS and ZnS-Ag nanoparticles. The spectra exhibit strong bands appearing in the 1112.93, 1249.87, 1352.10cm^{-1} correspond to ZnS nanoparticles [20].

FTIR study was carried out to identify the capping of the particles by glucose. The very strong peak at 1111cm^{-1} may be related to -C-O groups of glucose. The peak at 3664.75$cm^{-1}$is very broad and strong and can be assigned to the –OH groups from glucose. The IR study confirms the presence of –C-O and –OH groups of glucosewhich have a strong ability to bind metal .So we can infer that ZnS nanoparticles are encapsulated by glucose [3].

Antimicrobial Activity test: The antimicrobial activity of ZnS and ZnS-Ag nanoparticles wereinvestigated against MDR pathogenic bacteria, which were*Pseudomonas aeruginosa*, and *Staphylococcus aureus* as shown in table (2).

TABLE 2: The antimicrobial activity of ZnS and ZnS-Ag nanoparticles against pathogenic bacteria

ZnS *Pseudomonas aeruginosa*	ZnS , ZnS-Ag Concentration µgm/ml	MIC	ZnS-Ag *Staphylococcus aureus*	MIC
0.1 M	300	≤ 37 .5 µ gm	0.0005 M	300 µgm
	150		0.001 M	300 µgm
	75		0.002 M	75 , 150 µgm
	37.5 18.75		0.004 M	75 µgm
			0.008 M	75 µgm

The MIC of ZnS and ZnS-Ag nanoparticles against tested bacteria was observed visually. The results showed that *Pseudomonas aeruginosa* and*Staphylococcus aureus* were inhibited at 37.5µg/ml or less for ZnS; *Pseudomonas aeruginosa* and *Staphylococcus aureus* were inhibited at 75µg/ml of ZnS- Ag. The results obtained are better than the results that reported[20].By using chemical method to synthesis ZnS,ZnS-Ag nanoparticles that may be becausethe quantum dot size of nanoparticles with high stability as well as a very good biocompatible of the synthesized nanoparticles all these reasons increased the efficiency of nanoparticles.

CONCLUSION

ZnS and ZnS-Ag nanoparticles have been successfully synthesized by green routewhich is eco-friendly, using the microwave method with glucose as capping and stabilizing agent. This approachsupports the biocompatibility of synthesized nanoparticles. An average particle size of 3-2.8 nm was obtained using Debye Scherer formulain XRD spectra. The coating of the nanoparticles by glucose was confirmed by the FTIR spectroscopy.The MIC tests demonstrated that 37.5 µg/ml and 75µg/ml of ZnS NPs and ZnS- Agrespectively were the best antibacterial activity against both *P. aeruginosa* and *S. aureus*. In conclusion, the current green synthesized methods of ZnS and ZnS-Ag nanoparticles can be potential candidates for treating pathogenic bacteria and as a production agent against gram positive and gram negative bacteria.

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