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Synthesis of Colloidal Zinc Sulfide Nanoparticle Via Chemical Route and Its Structural and Optical Properties

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ABSTRACT : In this work ,the zinc sulfide(ZnS)Nanoparticles were synthesized by simple chemical route at room temperature by using Zinc Chloride powder $ZnCl_2$ and Sodium Sulfide powder Na_2S as basic materials, ZnSnanocrystals are measured by X-ray diffraction(XRD), Ultraviolet–Visible spectroscopy (UV-VIS)and fluorescence spectrophotometry. The optical properties and Structural of Nanoparticles have been investigated ,the results show that the high absorbance in near UV regions of spectrum ,while the grain size of ZnS nanoparticles calculate to be approximately (1.94- 2.75) nm from XRD test and optical energy gap of the nanoparticles is found to determine is range 3.8eV . Photo luminescence (PL) spectra of the samples give blue-light emission when the samples excited by UV light with wave length at 250 nm ,also in PL results give three bands emission (multiple peaks) are broad and strong where centered at three positions at 310nm,350nm and 400nm.

I. INTRODUCTION

Wide band gap of II-VI compound semiconductors such as CdSe, CdS, ZnS , etc., to be novel materials favorable for numerous applications of technological . In recent years, the nanosized semiconductors is the great interesting in all fields of the scientific and technological , Nanoparticles of semiconductors that use as light emitting diode, phosphors in lighting, displays, solar cell, X-ray sensors and window material, photocatalyst and electrochemical cell [1]-[9],the Zinc Sulfide (ZnS) is one of this family , that use in many applications in optoelectronics due to its credit ,with regard to an important phosphor for photoluminescence (PL), cathodoluminescence (CL) and electroluminescence (EL) devices because of its better chemical stability different from other chalcogenides [2,3] . ZnS crystallizes have the zinc-blende cubic (ZB) or wurtzite (WZ) structures at room temperature with a direct wind energy gap in the range of 3.68 eV or 3.77 eV, respectively [4].Many techniques can be used for preparingof (ZnS) nanoparticles ,such as soft chemical method,[5] chemical precipitation,[6] sol–gel method,[7]co-precipitation,[8]microwave irradiation method,[9]and colloidal microemulsion [10] , these methods are the most important due to their important nonlinear optical properties, as well as physical and chemical property that differ noticeably from features of ZnS as bulk, [11] semiconductor Quantum dots or nanocrystals (NCs) formed in colloidal solutions, these the nanocrystals have suspended in a solvent during the chemical preparation[12] In present work, we use a chemical method to preparation ZnS nanoparticles,this route was chosen due to its simplicity and inexpensive .The structural and optical properties were studied by XRD ,UV-VIS spectrum ,and PL analysis , the energy band gap values have been calculated by using the UV-visible spectrophotometry and fluorescence , the particle sizes have been obtained from XRD pattern.

II.EXPERIMENTAL WORK

A. Preparation of ZnS Nanoparticles

To prepare samples of ZnS nanoparticles by using the chemical method , it can be mixed two aqueous solutions , the first solution 0.1M Zinc Chloride powder $ZnCl_2$ (0.27g) dissolving in 20 ml distilled water ,put on stirrer to complete for 20 min , then added some drops from Ammonium hydroxide to the admixture in order to pH solution reaches to required level of (pH=8) at room temperature , while the another solution was obtained from using (0.156g) sodium sulfide powder dissolving Na_2S in20 ml distilled water .

The first,Na_2S Solution added drop by drop to $ZnCl_2$ solution ,the mixture of two solutions were mixed in a three-neck flask and were placed on magnetic stirrer at the room temperature ,it is mentioned that the argon gas are continued flowing through the synthesis for 3hours ,in the final step the ZnS NPs production white color precipitation

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this agreement with other researcher [13], X-Ray Diffraction (XRD) pattern of ZnS nanoparticles were measured by(SHIMADZU XRD-6000 X-ray diffractometer (CuKα radiation λ=0.154nm) in 2θ range from (20-80), The absorption spectrum of the samples is recorded by using OPTIMA SP-3000 supply by Optima Company,UV–VIS spectrophotometer covering a range from (200 – 1100) nm by using colloidal solution.The photoluminescence spectrum of ZnS colloidal solution is plotted using SL 174 SPECTROFLUOROMETER supply byELICO Company ,covering range from (200–600)nm.

III. RESULTS

A.X-Ray Diffraction study

The samples of colloidal ZnS nanoparticles measure by the XRD patterns as shown in the **Figure. 1**. Noticeably, the results that demonstrated the ZnS nanoparticles is cubic (wurtzite)and polycrystalline structure,depending on the synthesis conditions such as synthesis temperature and precursor concentration[14] Also ,found from XRD test three different peaks at diffraction angles (2θs): 28.36° , 48.3°and 56.45° respectively which proved that ZnS nanoparticles prepared with polycrystalline structure. The high intensity peak is oriented at lattice plane (111) whereas the other reflections located at (220) and (311) directions , the peaks positions and intensity dependent on synthesis temperature ,its noticed that the peaks are very broad and high intensity at room temperature , the grain size of nanoparticles (D) are measured by the debyeScherrer equation (1)[15] as following:

$$D = 0.9\lambda / \beta \ \text{Cos}\ \theta \qquad (1)$$

Where λ = 1.54056 °A is the wavelength of the incident ray(X-ray), D is the particle size, θ is the Bragg's angle and β is the full width at half maximum of the peak .

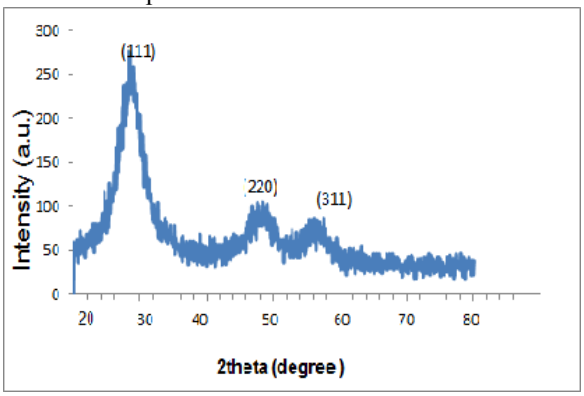

Figure 1 . The X-ray diffractions of the colloidal ZnS nanoparticles

Figure .1 illustrate that the peaks broadening may be give clearly proofing of the formation of the ZnS nanostructure and very small size depending on reaction condition ,elsewhere [16], as well as in [2] shows that broadening in the peaks in the XRD results was obviously and indicates that the ZnSnanocrystal are formed with very small size about (1.85-2.44nm). also ,it can be calculated particle size from the full width half maximum (FWHM)of (111) direction at angle 28.36° on 2theta (degree) scale by Scherrer equation , the value of particle size is measured to be around 2.75 nm . also ,in the same method can be found the other values as shown in Table 1

The solution of Zinc Chloride andSodium Sulfide were combined and with addition the second solution slowly and then the mixture put into magnetic stirrer at short time, in addition to pass Argon gas and stirrer, leading to decomposition ofSodium Sulfide, promoting a greater amount of nuclei which further gives greater concentration of particles in the dispersion and creates particles in small size.

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Table 1 .The table shows results values grain size of the nanoparticles which calculated from equation (1),diffraction of angle(2θ), the full width half maximum (FWHM), Miler indices (hkl).

No. of peak	Miler indices (hkl)	Bragg's angle(2θ) (degree)	FWHM β(degree)	COS(θ)	Grain size (D) nm
1	(111)	28.36	3.1211	0.9694	2.75
2	(220)	48.3	4.7110	0.9124	1.94

The particle size clearly depends on the synthesis condition ,where the size of particle decrease according totemperature and reaction time

B. Optical properties

➢ Absorption Spectrum

The samples of colloidal ZnS nanoparticles shows a well-known absorption properties at 325 nm,the peak position reflects the band gap of the nanoparticles ,as shown in **Figure 2** which illustrate high absorbance of ZnSNanocrytals in the ultraviolet region and low absorbance in the visible region , the absorption due to the electron excitation transition from VB to CB .Also the shift in the optical absorption spectrum is known to take place owing to strong quantum confinement effect caused by the reduction particle size, which occurs in the case of nanoparticles when the particle size becomes comparable with or smaller than Bohr radius of exciton [17]The shift towards shorter wavelength indicates an increase in the optical band gap. However; It can be used to determine magnitude of the optical energy gap of colloidal ZnS nanoparticles, this result agreement with another absorption spectra recorded by (C. S. Pathak and et. al and M. Dhanam and *et al.*) [18,19]

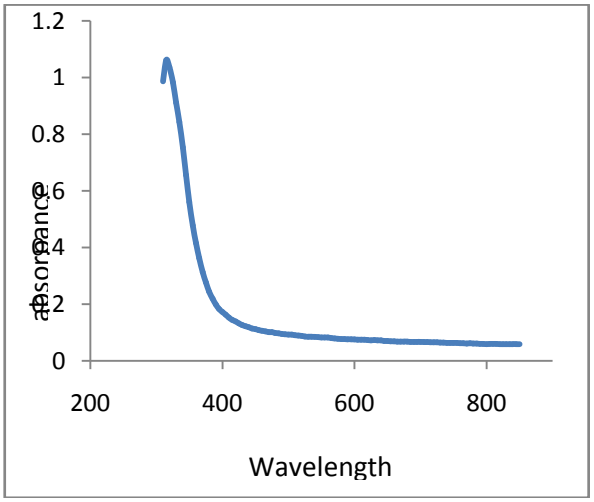

Fig:2 .UV-VIS absorption spectrum of ZnS nanoparticle.

By the absorption spectrum can be obtained on the energy gap of the ZnS nanoparticles , Tauc equation as in " (2)" that represented evaluate energy gap by plotting a graph between($\alpha h\upsilon)^2$ versus photon energy (hν) and by extrapolating the linear region of the curve to the energy axis ,as following [20].

$$\alpha h\upsilon \propto A(h\upsilon - E_g)^{1/2} \quad (2)$$

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Where α is the absorption coefficient, hυ is the photon energy, $E_g$is the direct band gap energy, and A is a constant. The **Figure 3** shows the relation between $(\alpha h\upsilon)^2$ versus hυ , where the intercept of the line gives the value of energy gap about 3.8 eV compare to the value of bulk ZnS of 337 nm (3.68 eV) [2]exhibits that energy gap increase with decrease grain size and blue shift of band edge .

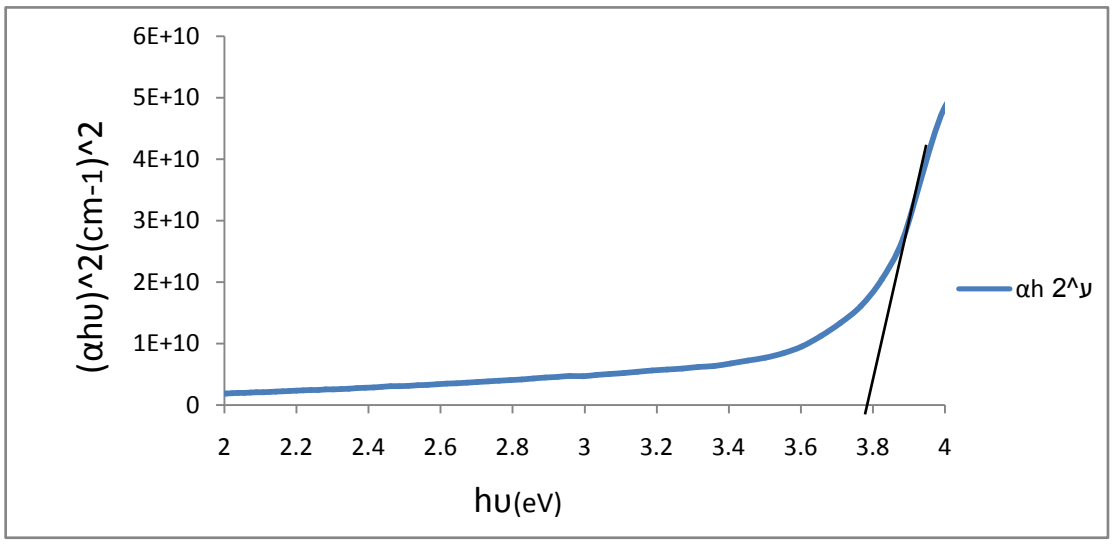

Fig. 3. the graph between $(\alpha h\upsilon)^2$ versus hυ of ZnS nanoparticles .

➢ The photoluminescence Spectrum

The photoluminescence analysis of the colloidal ZnS nanoparticles as shown in **Figure. 4 ,** the samples is excited by 250 nm line of UV excited . According to Some researcher [19] have explained that the PL spectra of ZnS nanoparticles may be belong to many reasons such as surface defects . The PL emission in ZnSnanocrystals due to existence of point defects ,sulfur vacancy and appearance of photogenerated by means of generation electron–hole pair is well defined excitons processes , in other words the electronic transitions from the valence band to conductance band[21,22]. In PL of ZnSnanocrystals can be observed three bands emission , first one is located at 310nm to determine an energy gap corresponding to 4 eVby "equation (3)"

$$E(eV) = 1240/\lambda\ (nm) \qquad (3)$$

Further, the another bands emission centered at 350 nm(3.5) and 400nm(3.1) is broad and strong because recombination between VB and sulfur vacancy associated to donor level or structural defects. Also, found that the sample exhibits PL emission in the blue region with multiple peaks indicate the involvement of different luminescence centers in the radiative process [15].

The PL properties depending on concentration of Zn and value of pH, in this work pH=8 effected to occur the strongest PL at higher pH is consistent with previous studies of similar NCs such as CdS[23], also pH is known to affect the surface characteristics of aqueous colloidal nanocrystals . The explanation was that surface trap states due to species

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like HS^- were converted into HO^- at higher pH, resulting in better surface passivation and thereby increased PL. The same explanation could apply to the current ZnSNCs[24].

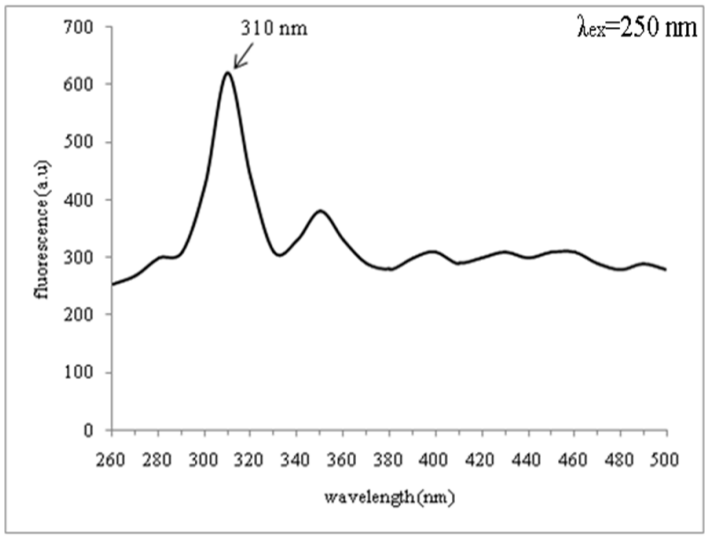

Fig 4 : The Photoluminescence spectra of colloidal ZnS nanoparticles at room temperature.

IV. CONCLUSION

ZnS nanoparticles that preparation chemical routeis simple technically and economically also, suitable for many applications as it can produce large amount of materials in short time . In recent years , the researchers interesting for topic synthesis of ZnS nanoparticle, the grain size were obtained from XRD analysis is found to be in the range 1.94-2.75nm while the band gap energy of ZnS NPs is found in the range3.8eV from absorption study and the blue shifted of absorption band from the bulk. PL emissions have been observed three peaks which excited by UVlight.

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Hanan has completed her Master and B.Sc from Baghdad University/ Physics Science. She is atutor atWassit university /college science /Physics department for ten years and she worked in workshop at same university to preparation nanoparticle with group from her colleagues . She has published more than 8 papers in reputed journals and has been working in nanotechnology group in university of Baghdad.