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Effect of High pH Variation on the Structural and Optical Properties ofZnS NanoparticlesPrepared by Chemical Route

[1]Ghaida. Salman,[2]Manal. Medhat and [3]Abdulkarim.Muhammed

[1]*PHD student, Department of physics, college of science, Baghdad University, Baghdad, Iraq.*
[2]*Professor, Department of physics, college of science, Baghdad University, Baghdad, Iraq.*
[3]*Asst. Professor, Department of chemistry, college of science, Baghdad University, Baghdad, Iraq.*

Address For Correspondence:
Ghaida. S. Muhammed, Baghdad University, Department of physics, college of science, Baghdad, Iraq.
E-mail: (1)ghaidasalman7@gmail.com.

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ABSTRACT:

ZnS nanoparticles have been synthesized by chemical route at room temperature between zinc chloride and sodium sulfide in aqueous solution as source materials at different PH (8, 9.5, and 12) respectively. The high pH variationgives an advantage on the structural and optical properties of ZnS nanoparticles.The characterization of the product is examined by X-ray diffraction method (XRD), UV-VIS absorption spectrophotometer, photoluminescence (PL) spectra, atomic force microscopy (AFM), and scanning electron microscopy (SEM). The crystalline size of ZnS nanoparticle samples are calculated from the XRD patterns for pH (8, 9.5&12) is (11.6, 14.5&12) nm respectively; while the average particle size obtained from the SEM is (16, 14,&10) nm. Also, from SEM images the ZnS nanotubes are observed at pH=12. The optical absorption spectra for different values of pH show a strong absorption with a tendency towards the blue shift. The room temperature photoluminescence spectra of the solution show peaks centered at (317,319 &322) nm, indicating an energy gaps of (3.85, 3.88 &3.95) eV respectively. Therefore, the increasing of pH causes the decreasing of nanoparticle size according to the SEM images. Hence, the decreasing of nanoparticle size tends to the increasing of the energy gap according to the quantum confinement effect.

INTRODUCTION

The needof miniaturization for the electronic devices nanotechnology isthat key for the novel properties of nano-materials. Research in nanoscale materials get started because of the unique properties that are obtained at this scale, by changing the shape or size of these materials. The change in properties of nanoscaled materials is due to the small length scale of the electron motion comparing to Bohr radius (Iftikar*et al*., 2014).This change resulting from quantum confinement, currently have more interested. Semiconductor nanoparticles exhibit size-dependent band gap energies, melting point, and solid-solid phase transition temperatures (J.P.Borah*et al*., 2008).ZnS has been widely studied as an important wide band- gap semiconductor (3.6 eV) (Zhongwu Wang *et al*., 2005). It is one of II–VI compound group, and one of the most promising materials because of its non-toxicity, and cheap (F. Haque*et al*., 2014). ZnSexist in two crystal structures, cubic (sphalerite) or hexagonal (wurtzite)(G. Murugadoss*et al.*, 2014). It is one of talented materials for blue light emitting laser diodes; electro luminescent displays films and the solar cells (L. Gayou*et al*., 2010).

The efficiency of hetero junction devices depends largely on the interfacial properties between absorber and buffer layers. The wider band gap allows high energy incident photons to reach the junction, enhancing the blue response of the photo electronic and therefore gives better efficiency(M. A. Jafarov*et al*., 2015). Sofar, extensive efforts have been made on the synthesis of low dimensional ZnS nanostructures, including nanoparticles,

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nanowires, nanobelts, noncable, and nanotubes. In comparison to the large amount of work on low dimensional nanostructures, there are relatively few reports on complex nanostructures, although these structures are very necessary for many applications (Yugang Zhang*et al*., 2007).In this work, ZnS nanoparticles synthesized at different pH, and the structural and optical properties are studied.

2. Experimental Work:

The zinc sulfide ZnS nanoparticles were prepared by mixing two chemical solutions of 0.1M.The first solution prepared by dissolving 1.36g of Zinc Chloride powder ($ZnCl_{2)}$in 100 ml distilled water. Sodium hydroxide was added to the mixture to adjust the pH of the solution to the required levels (8, 9.5 and 12).ThepH controlled the rate of the reaction due to the common ion effect (Nada K. Abbas *et al*., 2013), while the second solution is obtained by dissolving 0.78g sodium sulfide powder (Na_2S) in 100 ml distilled water. The two solutions arestirredat room temperature with continuous flowing of argon gas until the ZnS nanoparticles are formed according to the following chemical reaction (Rita Choudhury *et al*., 2014; Jyoti P. Borah*et al*., 2008):

$$ZnCl_2 + Na_2S \rightarrow ZnS + 2\,NaCl \quad (1)$$

The X-ray diffraction (XRD) pattern of the prepared ZnS nanoparticles samples for three pHvalues isrecorded. The X-ray diffractometer source is (CuKα) radiation line of wavelength of 1.54 ˚A in 2θ range from 20◦ to 60◦.In order to investigate the surface morphology and surface roughness, the atomic force microscopy test (AFM) observations is performed. The AFM images were analyzed with the Pro Scan software; the root mean square surface roughness values are calculated.Morphology and the particle sizewere examined by scanning electron microscope (SEM)at two magnification powers .The UV-VIS absorption spectrum of the prepared ZnS nanoparticles was measured. The absorbance of the samples is measured in the range (200-1200) nm.Photoluminescence spectrum (PL) of the samples was measured too.

RESULTS AND DISCUSSION

3.1 XRD studies:

The XRD patterns shown in Figure 1 indicate the presence of three prominent broad peaks in all the synthesized samples. These peaks are located around 2θ values of 28°, 47° and 56° corresponding to (111), (220) and (311) diffraction planes (JCPDS card, No. 96-110-1051), respectively indicating cubic structure for the synthesized nanocrystals. In addition, it is appeared from this figure, 2θ peaks located around 31°, 34° and 36°, 62°, 67°. These peaksare related to (100), (002), (101) (013) and (112) planes respectively, of hexagonal wurzite structure of polycrystalline ZnO (JCPDS Card, No. 96-900-4181).This result closely suggests partial oxidation of ZnS nanoparticles sample synthesized in low acidic medium (pH=8), and an approximately complete oxidation of ZnS nanoparticles in a strongly basic medium (pH9.5 and12).The peak broadening in the XRD patterns clearly indicates the formation of ZnSnanocrystals of small size(G. Murugadoss*et al*., 2014;KuldeepS.Rathore*et al*., 2008). The peak broadening is a significant on producingNanoparticle. The size of nanocrystals has been calculated using Debye-Scherrerequation (KuldeepS.Rathore*et al*., 2008).

The X-ray pattern peaks and their bandwidth are illustrated in table1. The table contains the corresponding grain size of the prepared nanoparticles measured according to the Scherrerequation (F. Haque*et al*., 2014; KuldeepS. Rathore*et al*., 2008; S. Kalyanasundaram *et al*., 2013; Dasari Ayodhy a*et al*., 2013). ZnS nanoparticle samples of pH (8, 9.5and12) have average crystallite size of (11.6, 14.5&12) nm respectively. It is clear from this relationship that the average particle size distribution depends on the reactant pH. When the pH of the samples increases the intensity of the ZnS (111) peak increases, i.e.increasing the crystallinity.This result has a good agreement with other researchers (I. Ahemen*et al*., 2013).

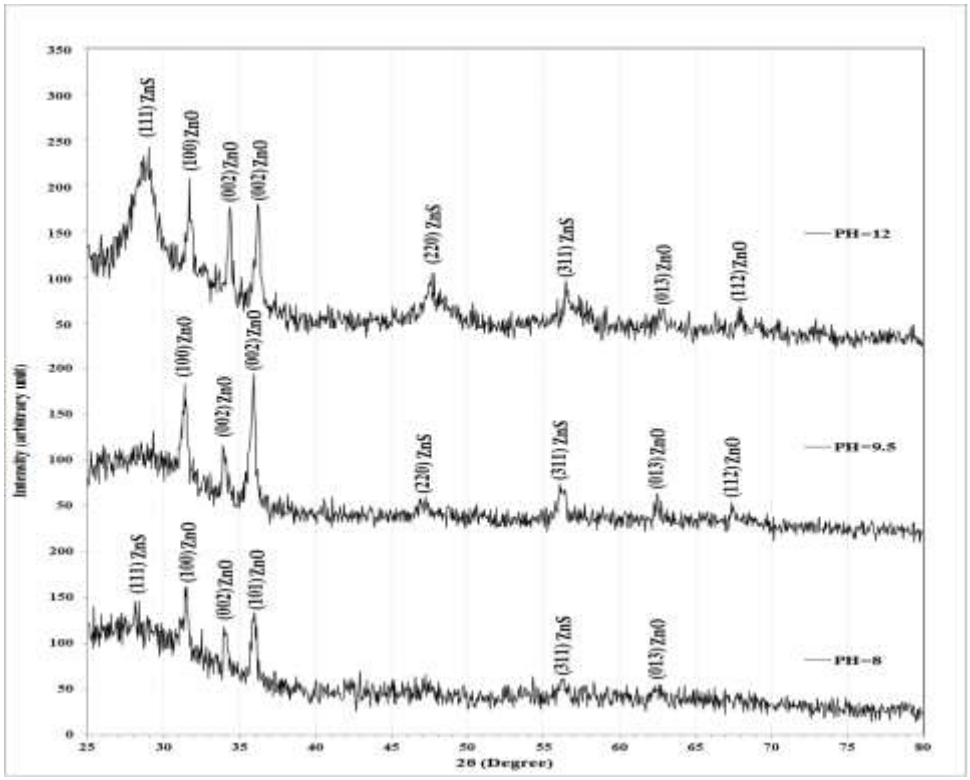

Fig. 1: The XRD pattern of the ZnS nanoparticle.

Table 1: The table illustrates the ZnS nanoparticles grain size, diffraction angle, Miler indices and FWHM of the diffraction peaks.

Table 1: X-ray diffraction pattern parameter of the ZnS nanoparticles.

pH	2θ (Deg.)	FWHM (Deg.)	d_{hkl} Exp.(Å)	G.S (nm)	hkl	d_{hkl} Std.(Å)	Phase	Card No.
8	28.100	0.9561	3.1730	8.6	(111)	3.1261	Cub. ZnS	96-110-1051
	31.450	0.6799	2.8422	12.1	(100)	2.8141	Hex. ZnO	96-900-4181
	34.050	0.5188	2.6309	16.0	(002)	2.6019	Hex. ZnO	96-900-4181
	35.900	0.4865	2.4995	17.2	(101)	2.4753	Hex. ZnO	96-900-4181
	56.200	0.9961	1.6354	9.0	(311)	1.6325	Cub. ZnS	96-110-1051
	62.300	1.6535	1.4891	5.6	(013)	1.4766	Hex. ZnO	96-900-4181
9.5	31.350	0.6245	2.8511	13.2	(100)	2.8141	Hex. ZnO	96-900-4181
	33.950	0.6037	2.6384	13.8	(002)	2.6019	Hex. ZnO	96-900-4181
	35.900	0.4245	2.4995	19.7	(101)	2.4753	Hex. ZnO	96-900-4181
	47.250	0.7201	1.9222	12.0	(220)	1.9143	Cub. ZnS	96-110-1051
	56.150	0.6888	1.6368	13.1	(311)	1.6325	Cub. ZnS	96-110-1051
	62.450	0.6265	1.4859	14.8	(013)	1.4766	Hex. ZnO	96-900-4181
	67.450	0.6327	1.3874	15.1	(112)	1.3781	Hex. ZnO	96-900-4181
12	29.000	1.9800	3.0765	4.1	(111)	3.1261	Cub. ZnS	96-110-1051
	31.700	0.5608	2.8204	14.7	(100)	2.8141	Hex. ZnO	96-900-4181
	34.350	0.4011	2.6086	20.7	(002)	2.6019	Hex. ZnO	96-900-4181
	36.200	0.4391	2.4794	19.0	(101)	2.4753	Hex. ZnO	96-900-4181
	47.500	1.2071	1.9126	7.2	(220)	1.9143	Cub. ZnS	96-110-1051
	56.450	1.0715	1.6288	8.4	(311)	1.6325	Cub. ZnS	96-110-1051
	62.850	1.4449	1.4774	6.4	(013)	1.4766	Hex. ZnO	96-900-4181
	67.900	0.5968	1.3793	16.1	(112)	1.3781	Hex. ZnO	96-900-4181

3.2 Surface morphology (AFM):

Atomic force microscopy technique (AFM) is a method to analyzefilmssurface topography. Figure2 (a, b) shows one dimensional and two dimensional AFM images for the ZnS films with different pH (8, 9.5 and 12) respectively deposited on glass substrate. Figure 2(c) represents the granularity accumulation distribution chart for them. The results indicates that the small average roughness (Sa), which indicate all films have smooth surface and display a granular structure. The surface roughness is the standard surface height profile deviation

from the average height. Since the grains wereexistingin different size, there is a surface roughness (Ali A. Yousif, 2015). The lowest surface roughness is for pH=12 and it may be attributed for high pH. Other topography parametersarethe root mean square roughness (Sq), average particle size, and ten point height (Sz) whichvalued from the granularity accumulation distribution, as shown in table2. From this figure, it can be noticedthat the ZnS nanoparticle films have high degree of homogeneity and the small grains have uniform distribution on the substrate. Also, it can be noticed the films uniformly deposited, and defects free and the morphology of these films are homogeneously distributed, which indicates the more film crystallinity.

Table 2: surface topography parameters obtained from AFM analysis for ZnS surfaces.

Sample	pH	Sa (nm)	Sq (nm)	Sz (nm)	Ave.G.S.(nm)
ZnS NPs	8.0	2.52	3.22	11.5	96.75
ZnS NPs	9.5	8.89	10.20	26.2	59.96
ZnS NPs	12.0	1.67	1.99	5.0	76.37

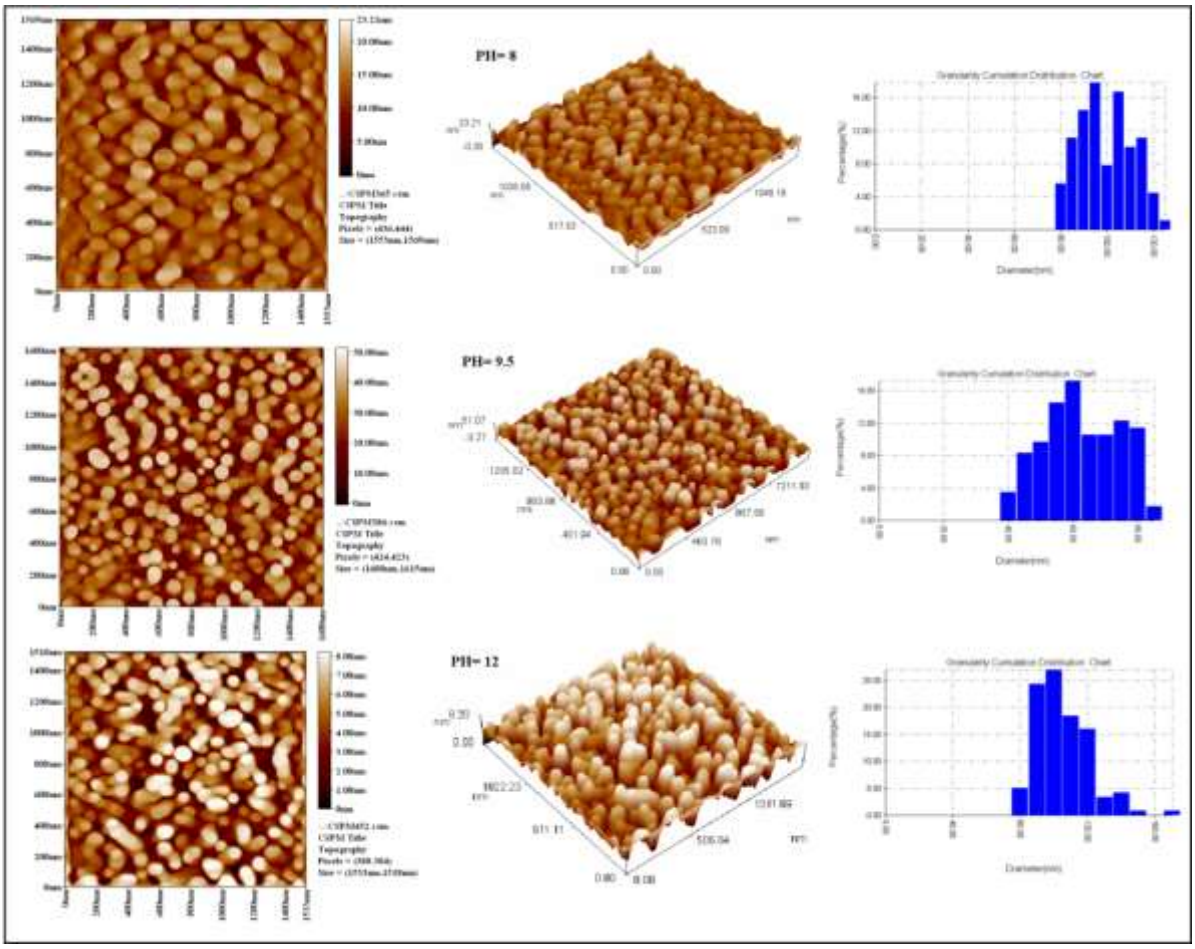

Fig. 2: AFM measurement of ZnS NPS surface deposited on glass substrate and for different pH and their granularity accumulation distribution of ZnS films.

3.3 Field Emission Scanning Electron Microscope (FESEM) Analysis:

Figure 3 illustrates ZnS nanoparticles images usingFESEM at two magnification powers. The distributions of grains are of irregular shape through all the regions. The qualities of such grown films are quite suitable for used inoptoelectronic devices (Bijoy Barman et.al. 2011).Also, the average particle size from the SEM is found to be(16, 14&10) nm.

The size of the particle is increased due to the agglomeration of the nanoparticles. In some places, various sizes of the particles (small and large size) are observed, i.e. nano-sized particles seem to be arbitrarily distributed in the films, and this observation is also seen by (IftikharM.Ali*et al*., 2014; John Rita *et al*., 2009).The formation of thenanotubes forpH=12is caused by the adsorption of OH^-ions on the surface.

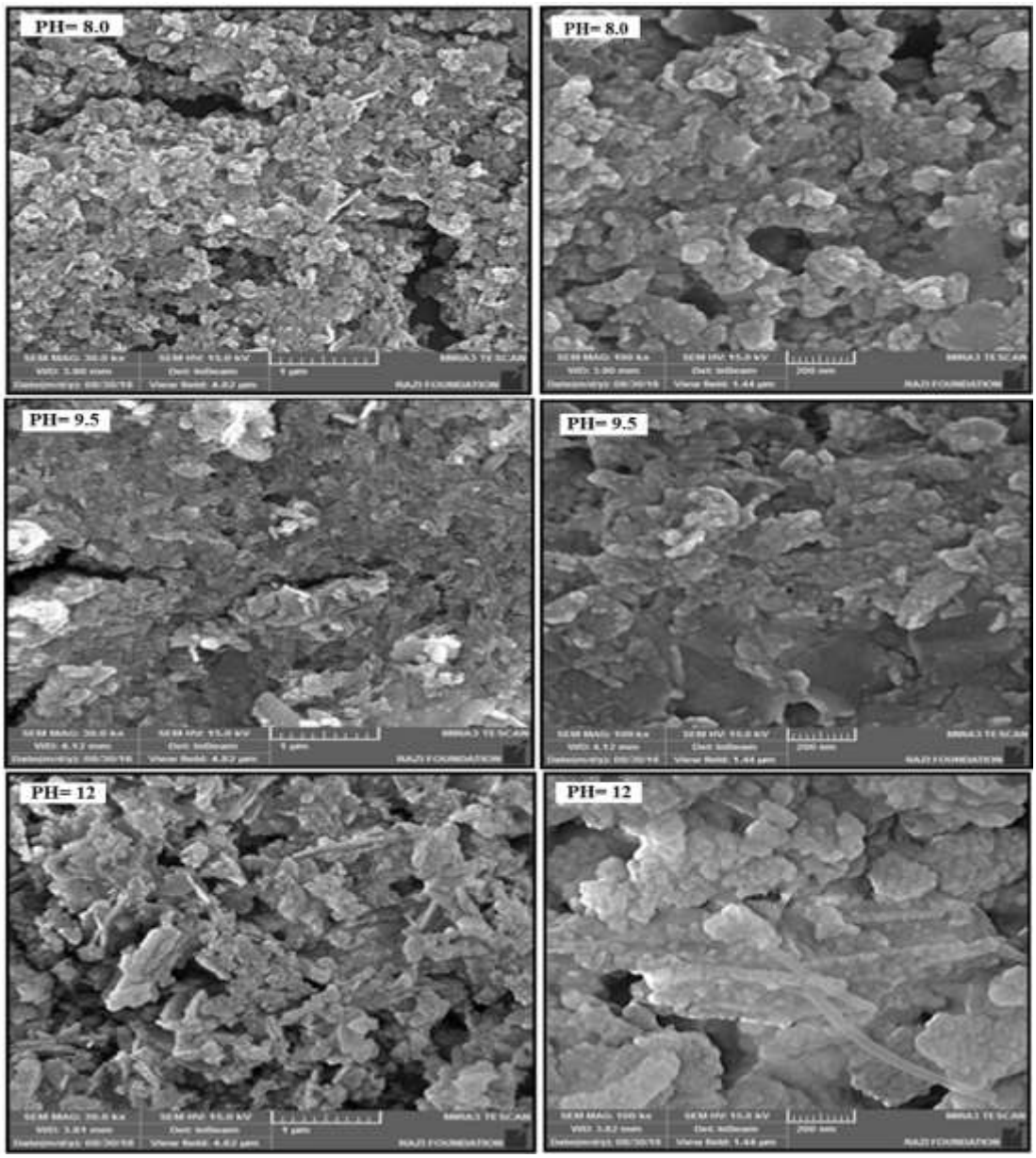

Fig. 3: ZnS nanoparticles samples by FESEM with (a) low magnification (left), (b) high magnification (right).

3.4 Optical Properties:

3.4.1 Absorption spectrum:

The absorption patterns of the ZnS nanoparticles in colloidal and for three pH (8, 9.5&12) at room temperature, were shown in Figure 4.

The optical properties of ZnS nanoparticles were determined from absorbance measurements in thewavelength range (200-1100) nm. The spectra show UV absorption excitonic peaks range (319-326) nm. The spectra show high absorbance of ZnS NCs in the ultraviolet; however, the absorbance at visible region is low. The linear part shows that the mode of transition is of direct nature (Nada K. Abbas *et al*., 2013; Jyoti P. Borah*et al*., 2008). The shoulder in absorption spectra corresponds to samples absorption edges. The absorptioncorresponds to excitation of electronsfrom the valence to conduction band, used to determine the optical energy gap for nanoparticles (Iftikhar M.Ali,*et al*., 2014).

It is clear from this Figure that all samples have absorption edge which has blue shift as compare with bulk ZnS for which the peak is at 345 nm. This shift due to the variation in nanoparticles size gets up from quantum confinement effect in the nanoparticles (Kuldeep S. Rathore*et al*., 2008). This shift is due to the excitons confinement, causing individual energy spectrum for nanoparticles. The effect impurity due to quantum confinement process depends mainly on the host crystal size. From figures of absorption; it can also be seen that there is no regular trend in the absorption intensity for the different samples (IftikharM.Ali*et al*., 2014).

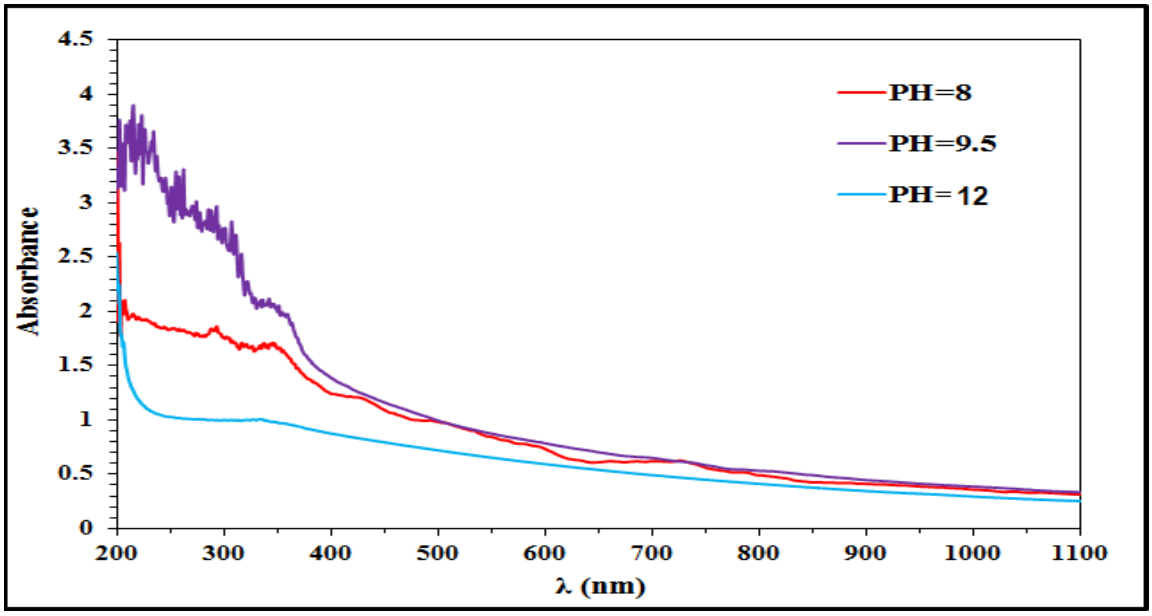

Fig. 4: UV-VIS absorption spectrum of ZnS nanoparticles films for different pH on glass substrate.

3.4.2 Photoluminescence Spectrum (PL):

The band gap and the defect states in the semiconductor from PL spectrum can be studied. Usually the value of the direct band gap determined from the photoluminescence peaks as in the relation bellow:

$$E\,(eV) = 1240 / \lambda\,(nm) \qquad (2)$$

The photoluminescence spectra (PL) of the ZnS nanoparticles for different pH were excited by 250 nm wavelength are shown in Figure5. It can be noticed from this figure, the band edge transition are centered around (317,319 and 322) nm, indicating an energy gaps of (3.85, 3.88 and 3.95) eV respectively. The other peaks centered at around (375 and 425) nm is attributed to the recombination between the sulfur-vacancy-related donor and the valence band. This emission is caused by recombination process of charge carriers in shallow traps. It is seen that when the size of the Nano particles decreases, the luminescence has been found to be dominated by the band impurity also, surface passivation by sulphur has resulted in reduced emission intensity of this band indicating involvement of surface defects (Jyoti P. Borah*et al*., 2008). Since pH is known to affect the characteristics of aqueous colloidal nanocrystals. Figure 5 shows the change of PL intensity for ZnS nanocrystals as a function of different pH values. Also, the PL clearly depends on pH with a noticeable increase in PL with increasing pH and a maximum PL at pH equal to (12) (Carley Corrado *et al*., 2009).

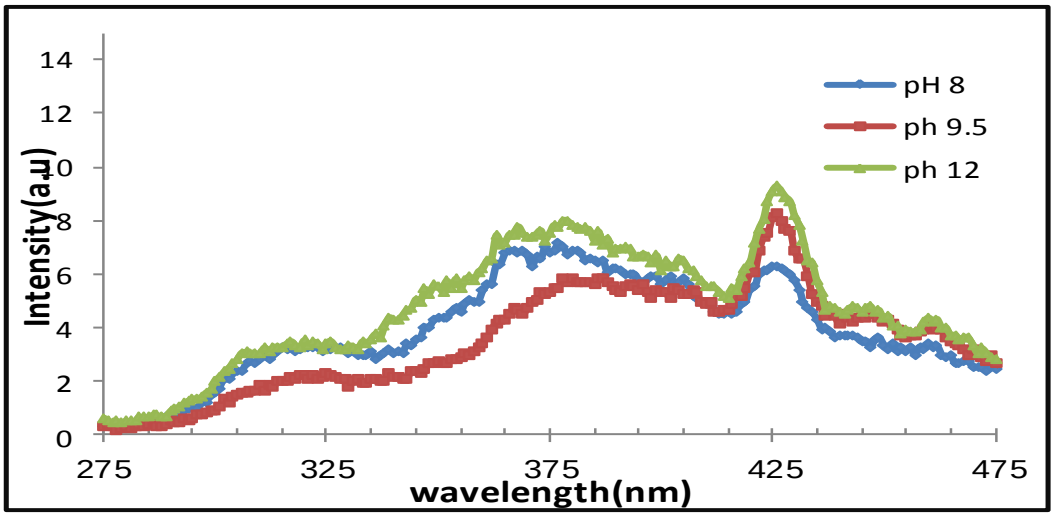

Fig. 5: PL spectra of the ZnS colloidal for different pH of solution.

Conclusion:

ZnS nanoparticles have been successfully synthesized by simple chemical route. XRD, AFM, SEM and PL studies reveal the formation of nanoparticles. The reduction of particle size with variation of pH in ZnS nanoparticles has been observed.

Future Work:

The effect of nanoparticle size and energy gap for ZnS nanoparticle on the efficiency of organic and hybrid solar cell are important to study as a future work.

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