

# Effect of High pH Variation on the Structural and Optical Properties of ZnS Nanoparticles synthesized by chemical route

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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 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 particle 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.

**KEYWORDS:** ZnS nanoparticles, PH, structural properties, photoluminescence.

## I. INTRODUCTION

The need of miniaturization for the electronic devices nanotechnology is that 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 [1]. 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 [2]. ZnS has been widely studied as an important wide band-gap semiconductor (3.6 eV) [3]. It is one of II–VI compound group, and one of the most promising materials because of its non-toxicity, and cheap [4]. ZnS exist in two crystal structures, cubic (sphalerite) or hexagonal (wurtzite) [5]. It is one of talented materials for blue light emitting laser diodes, electro luminescent displays films and the solar cells[6].

The efficiency of heterojunction devices depend largely on the interfacial properties between absorber and buffer layers. The wider bandgap allows high energy incident photons to reach the junction, enhancing the blue response of the photoelectronic and therefore gives better efficiency [7]. So far, extensive efforts have been made on the synthesis of low dimensional ZnS nanostructures, including nanoparticles, nanowires, nanobelts, nanocable, 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 [8]. In this work, ZnS nanoparticles synthesized at different pH, and the structural and optical properties are studied.

## Experimental

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). The pH controlled the rate of the

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reaction due to the common ion effect [9], while the second solution is obtained by dissolving 0.78g sodium sulfide powder ( $\text{Na}_2\text{S}$ ) in 100 ml distilled water. The two solutions are stirred at room temperature with continuous flowing of argon gas until the ZnS nanoparticles are formed according to the following chemical reaction [10, 11]:



The X-ray diffraction (XRD) pattern of the prepared ZnS nanoparticles samples for three pH values is recorded. The X-ray diffractometer source is ( $\text{CuK}\alpha$ ) radiation line of wavelength of 1.54 Å in  $2\theta$  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 was examined by scanning electron microscope (SEM). 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. Also, Photoluminescence spectrum (PL) of the samples is measured.

## II. RESULTS AND DISCUSSION

### 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  $2\theta$  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,  $2\theta$  peaks located around 31°, 34° and 36°, 62°, 67°. These peaks are 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 and 12). The peak broadening in the XRD patterns clearly indicates the formation of ZnS nanocrystals of small size [5, 12]. The peak broadening is a significant on producing Nano particles. The size of nanocrystals has been calculated using Debye-Scherrer equation [12].

The X-ray pattern peaks and their bandwidth are illustrated in table (1). The table contains the corresponding grain size of the prepared nanoparticles measured according to the Scherrer equation [4, 12, 13 & 14]. ZnS nanoparticle samples of pH (8, 9.5 and 12) 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 [15].

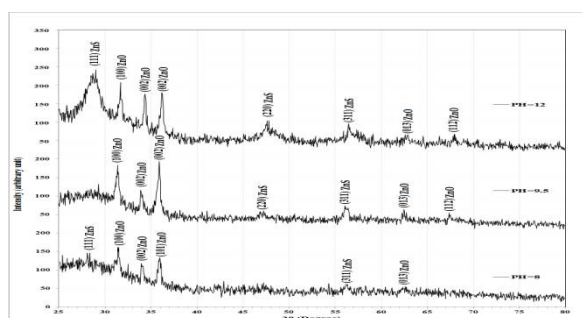


Figure 1: The XRD pattern of the ZnS nanoparticle

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Table 1, this table illustrates the ZnS nanoparticles grain size, diffraction angle, Miller 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	28.1	0.9561	3.173	8.6	-111	3.1261	Cub. ZnS	96-110-1051
	31.45	0.6799	2.8422	12.1	-100	2.8141	Hex. ZnO	96-900-4181
	34.05	0.5188	2.6309	16	-2	2.6019	Hex. ZnO	96-900-4181
	35.9	0.4865	2.4995	17.2	-101	2.4753	Hex. ZnO	96-900-4181
	56.2	0.9961	1.6354	9	-311	1.6325	Cub. ZnS	96-110-1051
	62.3	1.6535	1.4891	5.6	-13	1.4766	Hex. ZnO	96-900-4181
9.5	31.35	0.6245	2.8511	13.2	-100	2.8141	Hex. ZnO	96-900-4181
	33.95	0.6037	2.6384	13.8	-2	2.6019	Hex. ZnO	96-900-4181
	35.9	0.4245	2.4995	19.7	-101	2.4753	Hex. ZnO	96-900-4181
	47.25	0.7201	1.9222	12	-220	1.9143	Cub. ZnS	96-110-1051
	56.15	0.6888	1.6368	13.1	-311	1.6325	Cub. ZnS	96-110-1051
	62.45	0.6265	1.4859	14.8	-13	1.4766	Hex. ZnO	96-900-4181
	67.45	0.6327	1.3874	15.1	-112	1.3781	Hex. ZnO	96-900-4181
12	29	1.98	3.0765	4.1	-111	3.1261	Cub. ZnS	96-110-1051
	31.7	0.5608	2.8204	14.7	-100	2.8141	Hex. ZnO	96-900-4181
	34.35	0.4011	2.6086	20.7	-2	2.6019	Hex. ZnO	96-900-4181
	36.2	0.4391	2.4794	19	-101	2.4753	Hex. ZnO	96-900-4181
	47.5	1.2071	1.9126	7.2	-220	1.9143	Cub. ZnS	96-110-1051
	56.45	1.0715	1.6288	8.4	-311	1.6325	Cub. ZnS	96-110-1051
	62.85	1.4449	1.4774	6.4	-13	1.4766	Hex. ZnO	96-900-4181
	67.9	0.5968	1.3793	16.1	-112	1.3781	Hex. ZnO	96-900-4181

### Surface morphology (AFM):

Atomic force microscopy technique (AFM) is a method to analyze films surface topography. Figure (2 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 were existing in different size, there is a surface roughness [16]. The lowest surface roughness is for pH=12, and it may be attributed for high PH. Other topography parameters are the root mean square roughness (Sq), average

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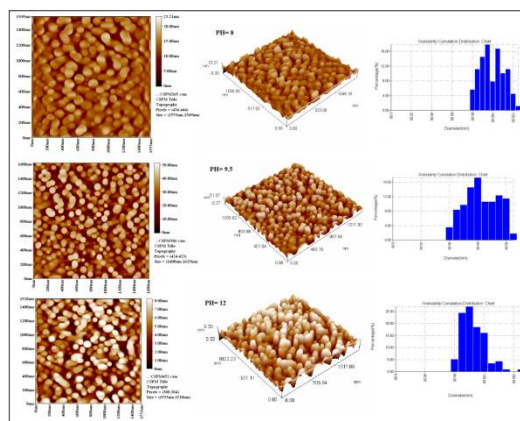
particle size, and ten point height (Sz) which valued from the granularity accumulation distribution, as shown in table (2). From this Figure, It can be noticed that the ZnS nanoparticle films have high degree of homogeneity and the small grains have uniform distribution on the substrate. Also, it can be noticed the films uniformly deposited, and defects free and the morphology of these films are homogeneously distributed, which indicates the more film crystallinity.

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**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	2.52	3.22	11.5	96.75
ZnS NPs	9.5	8.89	10.2	26.2	59.96
ZnS NPs	12	1.67	1.99	5	76.37



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

### Field Emission Scanning Electron Microscope (FESEM) Analysis:

Figure (3) illustrates ZnS nanoparticles images using FESEM 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 in optoelectronic devices [17].Also, the average particle size from the SEM is found to be (16, 14 &10) nm.

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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 [1, 18]. The formation of the nanotubes for pH=12 is caused by the adsorption of OH ions on the surface.

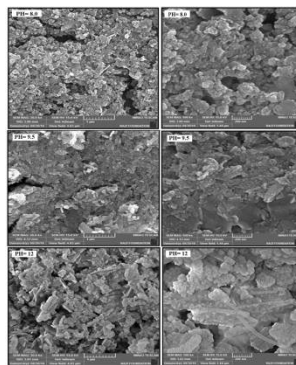


Figure 3: ZnS nanoparticles samples by FESEM with (a) low magnification (left), (b) high magnification (right).

## Optical Properties:

### a) 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 the wavelength 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 [9, 19]. The shoulder in absorption spectra corresponds to samples absorption edges. The absorption corresponds to excitation of electrons from the valence to conduction band, used to determine the optical energy gap for nanoparticles [1].

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 thenanoparticles [12]. 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 [1].

From the absorption peak the optical energy band gap of ZnS nanostructure has been calculated using the formula [9]:

$$E_g = h\nu_g = hc/\lambda_g \dots\dots\dots (1)$$

Where h is plank's constant and Eg is the energy band gap of the semiconducting nanoparticles in the optical spectra [9]. The calculated band-gap value of the anoparticles was 4.27 eV, which is blue shifted from that of bulk ZnS (Eg = 3.65 eV). Increasing of ZnS energy gaps could be an indication of the quantum confinement effect due to decreasing size of structures. These results are in agreement with other researchers [11, 12, and 17].

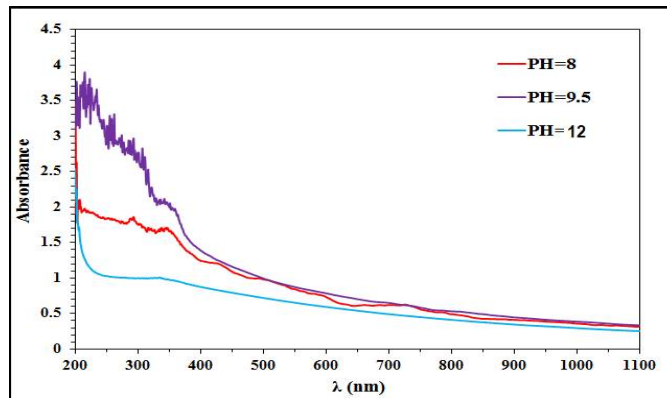


Figure 4: UV-VIS absorption spectrum of ZnS nanoparticles films for different pH on glass substrate.

**Photoluminescence Spectrum (PL):**

The photoluminescence spectra (PL) of the ZnS nanoparticles for different pH were excited by 250 nm wavelength are shown in Figure (5). 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 [11]. Since PH is known to affect the characteristics of aqueous colloidal nanocrystals. Figure (5) shows the change of PL intensity for ZnSnanocrystals 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) [20].

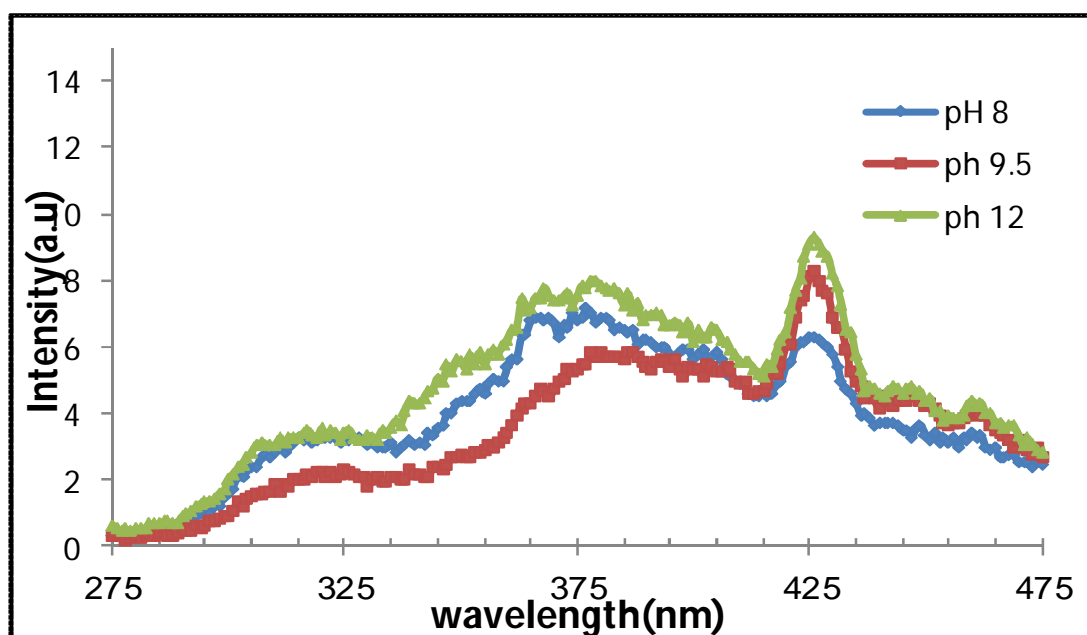


Figure 5: PL spectra of the ZnS colloidal for different pH of solution.



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## III. CONCLUSION

ZnS nanoparticles have been successfully synthesized by simple chemical route. XRD, AFM, SEM and PL studies reveal the formation of nanoparticles. UV spectra reveals that the absorption bands were blue shifted from the bulk. The PL clearly depends on pH with a noticeable increase in PL with increasing pH and a maximum PL at pH equal to (12). The reduction of particle size with variation of pH in ZnS nanoparticles has been observed.

1. An efficient edge detection scheme is applied to the greyscale image. The image I is blurred (to reduce false edges and over-segmentation) using open-close and close-open filters. The final blurred image Ib is the average of the outputs of these filters. The 3 x 3 8-connected structuring element of type 'square' is used here. Next, the morphological gradient operator is applied to the blurred image Ib resulting in an image G as follows:

$$G = \text{Dilation (Ib)} - \text{Erosion (Ib)}$$

The Morphological gradient is an edge-strength extraction operator that gives symmetric edges between foreground and background regions.

The resulting image is then thresholded to obtain a binary edge image. Global thresholding technique is used for that.

2. Closed edges in the binary edge image are grouped by dilation using eight- connected structuring elements. Then small connected components in the dilated image are filtered using erosion. The output is a binary image that contains text candidate regions.
3. Connected component labelling is performed to label each object separately.
4. After applying connected component labelling, the first set of criteria is applied which eliminate all objects whose area is greater than 10000 and filled area is greater than 8000. One more criteria namely major axis length is used which is used to retain the text region alone. All objects, whose major axis lengths are in between 20 to 3000, are considered to be text. To eliminate small objects, connected component labelling is applied to the resultant image and the second set of criteria is applied which eliminates all the objects whose area is less than 300 and filled area is less than 500.

After applying all these 4 steps, we get a filtered image that contains only text regions.

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