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New Method of Preparation ZnS Nano size at low pH

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Nano particles of zinc sulfide (ZnS) have been prepared by simple reaction between zinc chloride ($ZnCl_2$) and sodium sulfide (Na_2S) in aqueous solution at pH=3 as source materials .The characterization of the product was done by UV-VIS absorption, photoluminescence (PL) spectra, x-ray diffraction (XRD) and atomic force microscopy (AFM). The sizes of the sample as prepared were calculated by Debye-Scherrer formula according to XRD spectra. A UV-VIS optical spectroscopy study was carried out to determine the band gap of the nanoparticle ZnS to be about 4.27 eV. The room temperature photoluminescence spectra of the powder showed two peaks centered on 367 nm and 491 nm .The I-V characteristics are observed in dark and under illumination showing photosensitive nature of the ZnS powder.

Keywords: Nano particles of (ZnS), The characterization of (ZnS) :absorption, photoluminescence spectra, x-ray diffraction and atomic force microscopy

1. INTRODUCTION

Wide band gap II–VI semiconductors are expected to be the novel materials for the Optoelectronic devices. ZnS is an important member of this family and it has been extensively investigated [1] as it has numerous applications to its credit. ZnS has been used widely as an important phosphor for photoluminescence (PL), electroluminescence (EL) and cathode luminescence (CL) devices due to its better chemical stability compared to other chalcogenides material such as ZnSe. ZnS is a commercially important II–VI semiconductor having awide optical band gap, rendering it a very attractive material for optical application especially in nanocrystalline form .ZnS can have two different crystal structures (zinc blende and wurtzite),both of which are direct band structure [2,3].

In recent years, there has been considerable interest in semiconductors of nanometer dimensions due to the quantum size effect that they exhibit .Nanocrystalline semiconductors have electronic properties intermediate between those of molecular entities and macro crystalline solids and

are at present the subject of intense research . nanometric semiconductor particles exhibit novel properties due to the large number of surface atoms and the three dimension confinement of electrons[4].

2. EXPERIMENTAL

ZnS nanoparticles of ZnS were synthesized from ZnO .By adding 100 ml dishwater to 5 gm ZnO with stirring using magnetic stirrer at room temperature .Then dropping dil HCl (1:1) till complete dissolution to get a transparent solution .The PH was found to be 3.

1 wt% Na2S was added slowly till the whole solution appears completely milky. The chemical reaction occurs as follows

$ZnO + 2HCl \rightarrow ZnCl2 + H2O$…….(a)

$ZnCl_2+Na_2S \rightarrow ZnS +2NaCl$ ……..(b)

PH controlled the rate of reaction due to the common ion effect. At higher PH ,the solubility product increases .and an result no formation of ZnS particle is formed . The resulting solution was a slightly cloudy white. The white color indicated the formation of ZnS nanoparticles [5]

The resulting powder was washing, centrifuged, and finally dried at 80 °C .The nano-particles were collected by centrifugation at 2000 rpm for 15 minutes, and washed about three times. Further purification was made by ultrasonic bath.

X-ray diffraction was recorded with an automated X'pert Philips diffractometer with Cu Kα radiation beam λ=1.5406 ˚A .The optical absorption measurements obtained from the colloidal solution were performed in UV-Vis spectrophotometer SP-3000 plus ,OPTIMA INC. Japan .In order to investigate the surface morphology and surface roughness, the atomic force microscopy (AFM) observations were performed using an SPM model AA 3000 ,Angstrom Advanced Ins.,USA . The AFM images were analyzed with the Pro Scan software, calculating the root mean square surface roughness value. I-V characteristic is recorded using Keithley 6514 system electrometer and with Hioki 7020 variable power supply.

3. RESULTS AND DISCUSSION

3.1 XRD studies

The crystalline nature of the prepared nanosize ZnS powder is evident from the x-ray diffraction pattern (Fig.1).The most significant feature within the observed pattern, at 2θ=28.6264 , is assigned to the (111) reflection of the cubic zinc blende structure of ZnS (JCPDS No 5-566) .Two other prominent features are observed at 2θ = 47.7355 and 56.5339 ,which belong to (220) and (311)

reflections. No peaks from any other impurities such as ZnO or other compounds are detected.Our results are agree with [4,6,7] . From the x-ray patterns the broadening of the diffraction peaks of the nanoparticles is obvious [3,4,8]which is characteristic of nanosized by applying Debye- scherrer formula [9,10].

$$D= \frac{0.9\lambda}{\beta \cos\theta} \text{.....(1)}$$

Where D is the mean particle size, λ is the wavelength of incident X-ray (1.5406 ˚A), θ is the degree of the diffraction peak , and β is the full width at half maximum (FWHM)of the XRD peak appearing at the diffraction angle θ. The broadening of the absorption spectrum could be due to the quantum confinement of the nanoparticles. The mean calculated crystallite size of the ZnS nanoparticles shows that the synthesized nanoparticles are in the quantum confinement regime as shown table (1) .Thus, these nanoparticles may also be called the quantum dots.

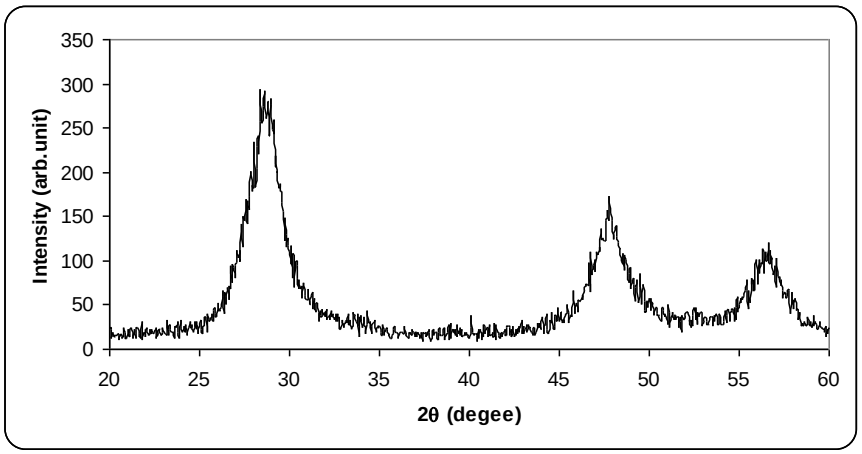

Figure 1. XRD of ZnS nanoparticle.

Table 1. Crystallite size of ZnS nanopartcles

No. peak	$2\theta_{(deg)}$ Exp.	FWHM (β)	$d_{Exp.}$ (A^o)	I/I_o Exp.	(hkl)	crystallite size(nm)
1.	28.6264	2.0875	3.1158	100	(111)	3.99
2.	47.7355	1.9875	1.9037	47	(220)	4.47
3.	56.5339	1.7167	1.62655	28	(311)	5.32

3.2 Optical properties

The optical properties of ZnS nanoparticle are determined from absorbance measurements in the range of 200-1100 nm. Fig. 2 shows the UV-visible absorption spectra of nanopar-ticle ZnS at the room temperature. The spectra show UV absorption excitonic peak at 290 nm indicating amonodispersed size distribution of particles.

The linear part shows that the mode of transition in this powder is of direct nature [11].

The band gap energy in a nanomaterial could be obtained from the absorption maxima. According to quantum confinement theory, electrons in the conduction band and holes in the valence band are spatially confined by the potential barrier of the surface. Due to confinement of both electrons and holes, the lowest energy optical transition from the valence to conduction band will increase in energy, effectively increasing the band gap (Eg) [12]. The shoulder or peak of the spectra corresponds to the fundamental absorption edges in the samples, and could be used to estimate the band gap of the nanomaterial [13].

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

$$E_{gn} = h\nu_{gn} = hc/\lambda_{gn} \quad \ldots\ldots\ldots\ldots\ldots (2)$$

where h=plank's constant and *Egn* = energy band gap of the semiconducting nanoparticles in the optical spectra .The calculated band-gap value of then anoparticles was 4.27 eV, which is blue shifted from that of bulk ZnS (340 nm, Eg = 3.65 eV). Increasing of band gap energies of ZnS nanostructures could be an indication of the quantum confinement effect due to decreasing size of structures.

The average particle size present in the nanocolloid can be determined by using the mathematical model of effective mass approximation [2,12,13]

$$\Delta Eg = [\ h^2/8\mu r^2] - 1.8e^2/\varepsilon_o\varepsilon_r r \quad \ldots\ldots\ldots\ldots (3)$$

where $1/\mu = 1/m_e^* + 1/m_h^*$ is the reduced mass of electron hole effective mass, $m_e^* = 0.34m_0$ and $m_h^* = 0.23m_0$ and $\varepsilon_r = 8.76$ is the permittivity of the sample.

The above equation derived, describes the particle size (r , radius) as a function of peak absorbance wavelength (λp) for ZnS nanocrystals [14].

$$r(nm) = \{-0.2963 + (-40.1970 + 13620/\lambda_p)^{1/2}\}/\{-7.34 + 2481.6/\lambda_p\} \quad \ldots\ldots (4)$$

The particle size obtained from this sample is 3.8 nm,which is good agreement determined by XRD. Our results are agree with [14].

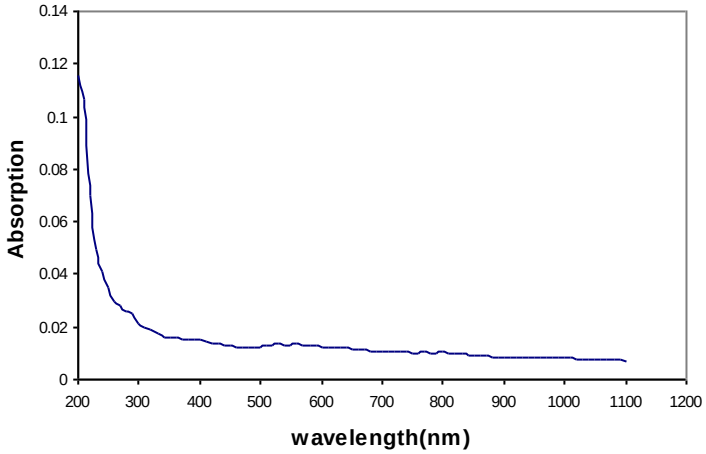

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Figure 2. UV-Vis absorption spectra of ZnS nano-particles.

3.3 PL Study

PL measurements then yielded information about ban gap energies of nanostructures that can be tuned by varying their sizes and the energetic positions of the electronic states in the band gap. On the other hand, wide band gap semiconductors are ideal materials for studies on trap states. Such localized states can be due to various types of imperfections like vacancies, interstitial atoms and dangling bonds. Bulk ZnS has a wide direct band gap of 3·68 eV. The large exciton binding energy (40 meV) is much higher than thermal energy at room temperature (~26 meV), the band edge PL of ZnS at room temperature is observed in high quality crystal [15].

PL at RT spectra are recorded with 250 nm excitation wavelength.Fig.3. Shows the emission spectra and from the data we have seen a strong emission bands at about 367 nm (3.37 eV) and other weaker peak was observed at 491 nm (2.5) eV.

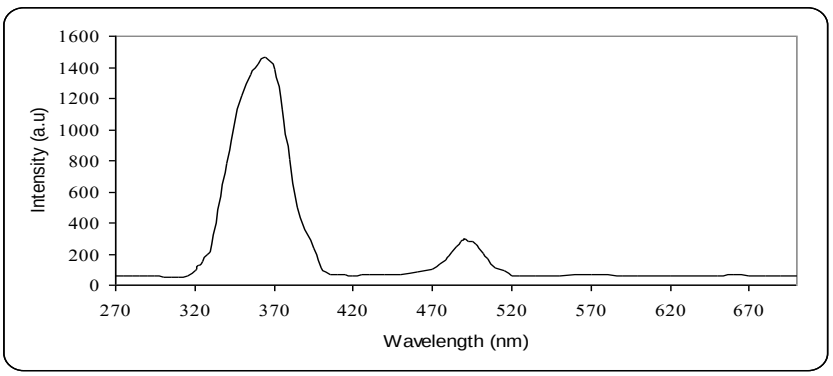


Figure 3. PL spectra of the ZnS nanoparticles prepared at pH =3

Usually for semicon-ductor nanocrystals, two emission peaks can be observed- the exciton and the trapped lumenescence [16,17].The exciton emission peak is sharp and the trapped emission is

broad [18,19]The emission bands showed in the spectra can be attributed to band gap emission and the strong band gap emission demonstrates the high crystalline nature of the as-synthesized particles[10].

The emission at 491 nm may be caused by the transition from the conduction band to the zinc vacancies V_{Zn} level (this localized vacancy level is above the valence band at 1.1 eV). The peak at 367 nm (3·37 eV) can indicate exciton recombination .Our results are agree with [15]**.**

3.4 I-V Characteristics

I-V characteristics of nanostructure ZnS powder are shown in Fig. 4. Both dark current and current under illumination increase linearly for both positive and negative applied bias up to ±1V.

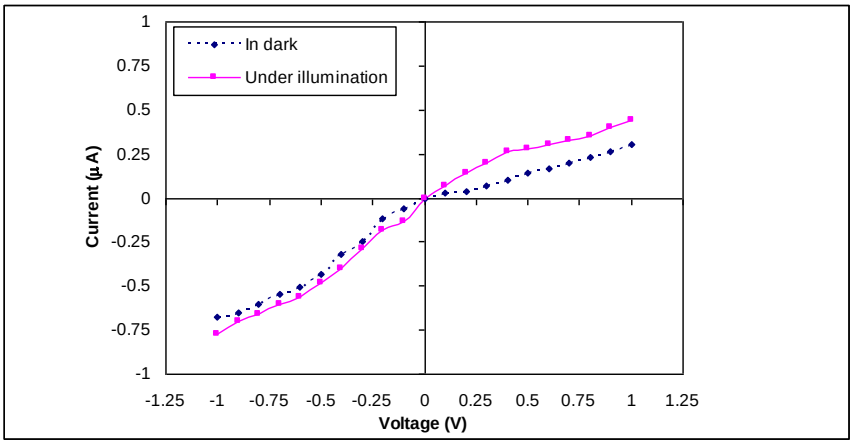
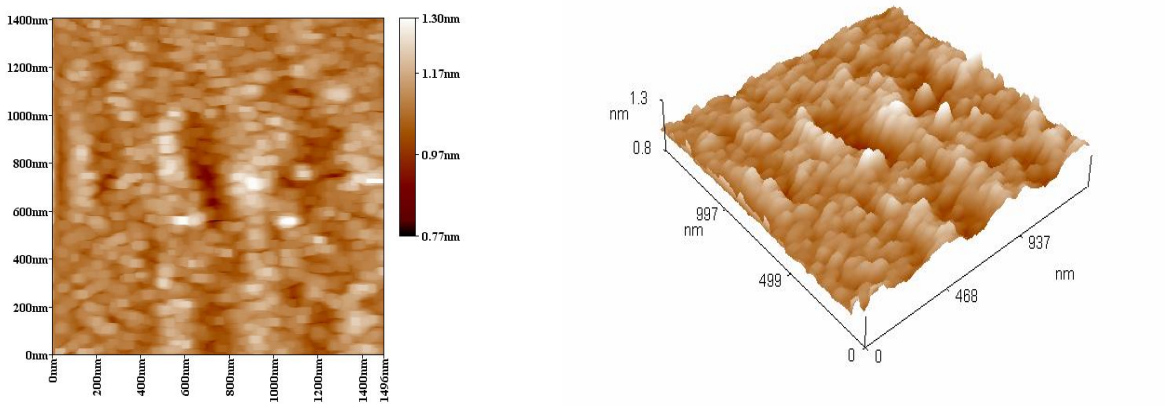


Figure 4. Current vs. voltage plots in dark and under illumination for a ZnS nanoparticle

3.5. Surface morphology



A B

Figure 5. AFM images of ZnS powder placing on glass. (a) Two-dimensional and **(b)** three – dimensional.

Atomic force microscopic (AFM) allows us to get microscopic information on the surface structure and to plot topographies representing the surface relief.

This technique offers digital images which allow quantitative measurements of surface features, such as root mean square roughness, *Rq*, or average roughness *Ra*, and the analysis of images from different perspectives, including three-dimensional simulation [9].

Fig.5 illustrates two and three dimensional AFM images of the ZnS .AFM measurement obtained by placing a drop of colloidal solution on glass.

As observable, average grain size of 72.92 nm in diameter. The root mean square roughness (*Rq*) and the average roughness (*Ra*) were found to be .053 nm and .048 nm, respectively. It is important to note that these obtained values are averaged and there is a statistical variation associated with them, which depends on the location of the measurements that are performed on the samples [20].

Tables .2 represent the Information of diameter, cumulation % and volume % of Zns nanoparticle and figure 6 its distribution chart.

Table 2. The Information of diameter, cumulation % and volume % of Zns nanoparticle

Diameter(nm)<	Volume(%)	Cumulation(%)	Diameter(nm)<	Volume(%)	Cumulation(%)	Diameter(nm)<	Volume(%)	Cumulation(%)
50.00	7.41	7.41	70.00	10.19	44.44	90.00	5.56	84.26
55.00	6.48	13.89	75.00	9.26	53.70	95.00	8.33	92.59
60.00	5.56	19.44	80.00	12.96	66.67	100.00	1.85	94.44
65.00	14.81	34.26	85.00	12.04	78.70	105.00	5.56	100.00

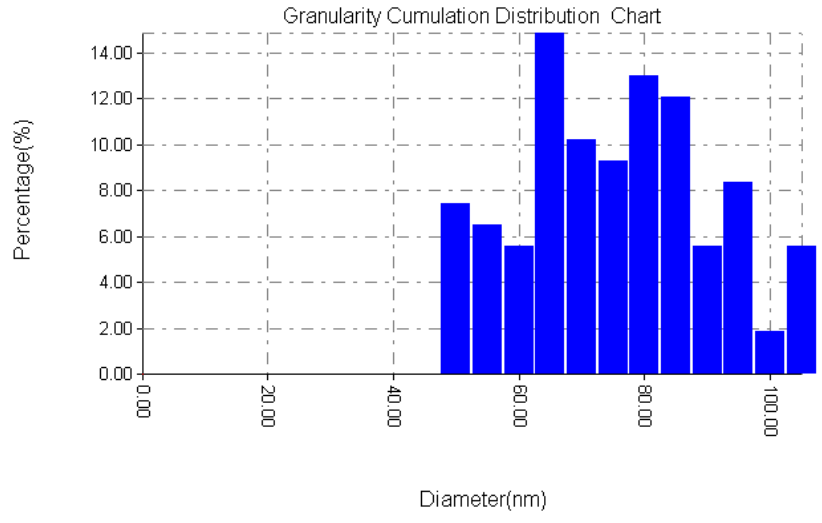


Figure 6. Mean particle size and particle distribution

4. CONCLUSION

In conclusion, we have successfully synthesized the ZnS nanoparticles by a simple aqueous chemical method using pure aqueous route resulting in primary particle sizes average about 4.6 nm. This particle size was calculated from the Debye- Scherrer formula. AFM image is used to study the

morphology of the synthesized nanoparticles. UV spectra revealed that the absorption band was blue shifted from the bulk. Photoluminescence investigation evidenced the high crystalline nature of the ZnS nanoparticles**,** and study I-V characterized.

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