Libyan Journal of Science & Technology 11:2 (2020) 00–00

Faculty of Science - University of Benghazi

Libyan Journal of Science & Technology

journal home page: www.sc.uob.edu.ly/pages/page/77

Absorption Spectra and Band gap of Thin Film NanocrystallineZnS Semiconductor Deposited at The Water/Toluene Interface

Enteisar M. Albrasi*; Hanan K. Bokhamada

Department of Chemistry, Faculty of Education, University of Benghazi, P.O.Box 3188, Benghazi-Libya

Highlights

- **Wet chemical method for preparing ZnS nanocrystalline.**
- **Deposition thin films of ZnS nanocrystalline at the water/Toluene interface.**
- **Absorption Spectra and band gap of thin films of ZnS nanocrystalline at the interfacial region.**

ARTICLE INFO

Article history:
Received 22 March 2020
Revised 17 May 2020
Accepted 00 June 2020

Keywords:
Thin-film; Nanoparticles, ZnS semiconductor; Liquid/liquid; Bandgap.

**Address of correspondence:*
E-mail address: albrasientesir@gmail.com
E. M. Albrasi

ABSTRACT

This work presents a wet chemical synthesis method that uses the interface of two immiscible liquids for the formation of a thin film of nanocrystalline ZnS semiconductor at 60°C.ZnS semiconducting colloid nanoparticles, containing cysteine as a capping agent was deposited as a thin film at the water- toluene interface. In this method, the capped ZnS with cysteine held in contact with toluene containing octylamine. The thin film produced was characterized by UV-visible spectroscopy. The UV-Visible absorption spectra are carried out to determine the bandgap of ZnS colloid nanoparticles and a nanocrystalline thin film of ZnS. From optical absorption measurements, it is clear that the direct energy gap decreases from 3.92-3.82 eV, and the size of ZnS colloid nanoparticles and nanocrystalline thin film calculated from the bandgap energy have been in the range of 3.7 - 4.2 nm.

1. Introduction

Transition metals chalcogenide including ZnS, CdS, CuS, NiS and PbS have been extensively studied and have attracted considerable attention in the last couple of decades due to their valuable properties and uses in different devices (Cushing *et al.*,2004; Rao.C.N.R *et al.*, 2005; Burda *et al.*, 2005). They are wide bandgap semiconducting materials and have extensive applications in laser, photo devices solar cells (Akimov *et al.*, 2010;Koh *et al.*, 2010; Huynh *et al.*, 2002; McDonalds., 2005) and electro-optical devices (Lodahl *et al.*, 2004; Achermann *et al.*, 2004) as well as biological sensors (Anker *et al.*, 2008; Mattoussi *et al.*, 2000; Geriou *et al.*,2002) because of their electronic and optical properties.

Among these metal chalcogenide, Zinc sulphide (ZnS) is one of an important II-VI semiconductor material and it has two crystal structures i.e. hexagonal wurtzite structure, having optical band gap 3.77 eV, and cubic zinc blende structure with 3.72 eV bandgap, whereas both hexagonal wurtzite and cubic zinc blende, have a direct wide bandgap of 3.68 eV (La Porta *et al.*, 2014; Tiwary *et al.*, 2014). ZnS has been used widely as phosphor for photoluminescence, electroluminescence (Choudapura *et al.*, 2019) and cathode luminescence devices because of it's better chemical stability compared to other semiconductor chalcogenides (Rinu Sam., 2017; Rahdar *et al.*, 2013). Zinc sulphide in nanoscale has unique properties such as the quantum size and enhanced surface to volume ratio, which makes it very useful for the chemical industry (Shaoqin and Zhiyong, 2010).

ZnS nanoparticles have been created using several methods like solid-phase reaction (Kaito *et al.*, 1987), sol-gel (Stanic *et al.*, 1997), spray pyrolysis method (Okuyama *et al.*, 1997), green reaction synthesis (Senapati *et al.*, 2013), organic chemical vapor deposition (Seo *et al.*, 2005), chemical bath deposition method (Roy *et al.*, 2006), chemical spray pyrolysis (Hernandez-Fenollosa *et al.*, 2008), successive atomic layer adsorption and reaction (Pathan and Lokhande, 2004), and liquid-liquid interface method (Fan *et al.*, 2007).

Liquid-Liquid interface to assemble nanocrystalline has been studied (O'Brien and Nomura, 1995). Because of the quality of the medium, and the assembly which is less prone to defects and cheaper than the assembly using other techniques. Newly, the interfacial region of two immiscible liquids such as water and oil has started as a powerful new medium for self-assembly of nanoparticles. (Duan *et al.*, 2004; Mezan *et al.*, 2018). The latest studies have shown that nanocrystalline thin films are formed at the interface of two immiscible liquids when metal precursors in the organic phase react with sulphide ions in the aqueous phase (Agrawal et al., 2005; Rao.C.N.R *et al.*, 2005; Agrawal *et al.*, 2006; Prabhakar *et al.*, 2018). Here in this research, we briefly report the preparation of ZnS nanocrystals at the water- toluene interface. The method includes sols of ZnS and toluene containing octylamine, the reaction occurs at 60°C yielding white nanocrystalline films of ZnS at the interfacial region.

2. Experimental part

2.1 Chemical reagents

In our experiments, all the chemicals that will be mentioned later are of analytical grade without further purification. Distilled

 ISSN 2663-1407; National Library of Libya, Legal number: 390/2018

water was used for all dilution and sample preparation. The chemicals, Sodium hydroxide pellet s(NaOH) and sodium sulfide (Na_2S) obtained from T-Baker Lab Chemicals, India, Zinc Chloride anhydrous ($ZnCl_2$) from Clariant Chemicals India, pure toluene (C_7H_8) from BDH Chemicals Ltd Poole, England, octylamine ($C_8H_{19}N$) and cysteine ($C_3H_7NO_2S$) from E.Merck Chemicals, Darmstadt Germany. UV-vis spectra of both ZnS samples were recorded by CE7400-7000 3ERIES Double Beam UV-vis Spectrophotometer manufacture Buck scientific, Inc.

2.2 Synthesis of Zincsulphide sols

Nine mg of $ZnCl_2$ in 50 ml of water was mixed with aqueous solution 20 ml containing 6 mg of cysteine using as a capping agent and stirred for 15 min at room temperature. The pH was adjusted to 10-11 using a few drops of 3%NaOH and 0.013 gr Na_2S in 20 ml water was introduced, the resulting mixture was stirred at room temperature for 3 hours utilizing a magnetic stirrer to get white sol, which displayed in (Fig. 1).

Fig. 1. photograph shows the preparation of ZnS colloid in the presence of a capping agent.

2.3 ZnS thin films

Zinc sulfide film was prepared by layering 20 ml of ZnS Sols was stood in contact with 20 ml of toluene containing 1 mmol of octylamine in the beaker. The beaker was left in the oven at 60°C for 3 hours. The white color had formed at the interfacial region of water and toluene as a result of ZnS deposition, by drafting upper layer thin film was transferred on the glass substrate (Fig. 2).

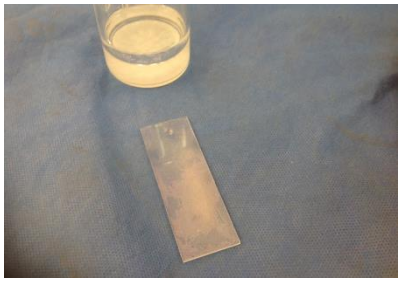

Fig. 2. Photograph shows of ZnS thin film formed at the water/toluene at 60°C.

3. Results and Discussion:

The absorption spectra of ZnS Sols and thin film are shown in Fig. 3(a) and (b). It is evident that the absorption peaks for ZnS colloid and deposited film at the interface are obtained at 316 and 324 nm respectively, suggesting that blue shift compared to the value of bulk (336 nm) the change to higher energy indicates to the crystallites have quantum confinement.

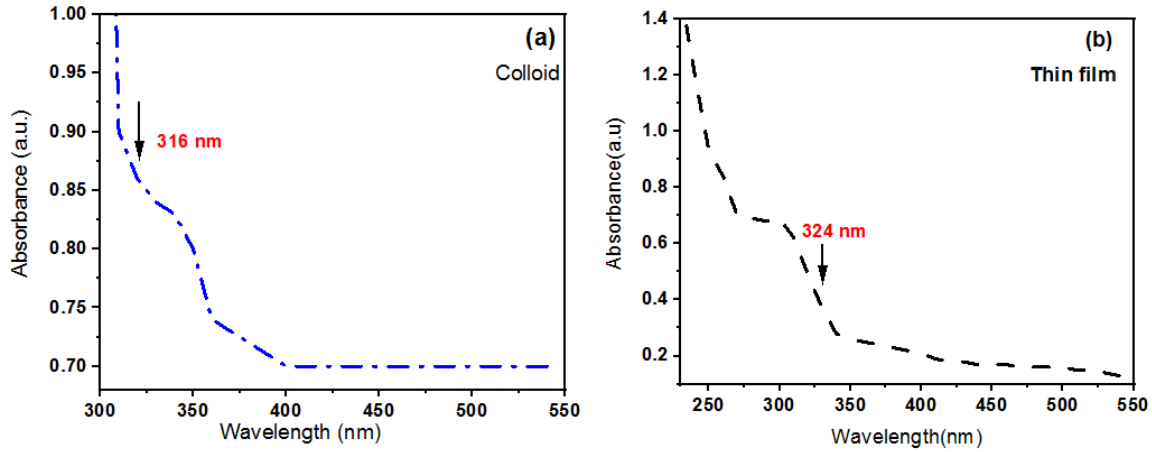

Fig. 3. Exhibits (a) the electronic absorption spectra of ZnS Sols at room temperature, (b) ZnS film at the interfacial region at 60°C.

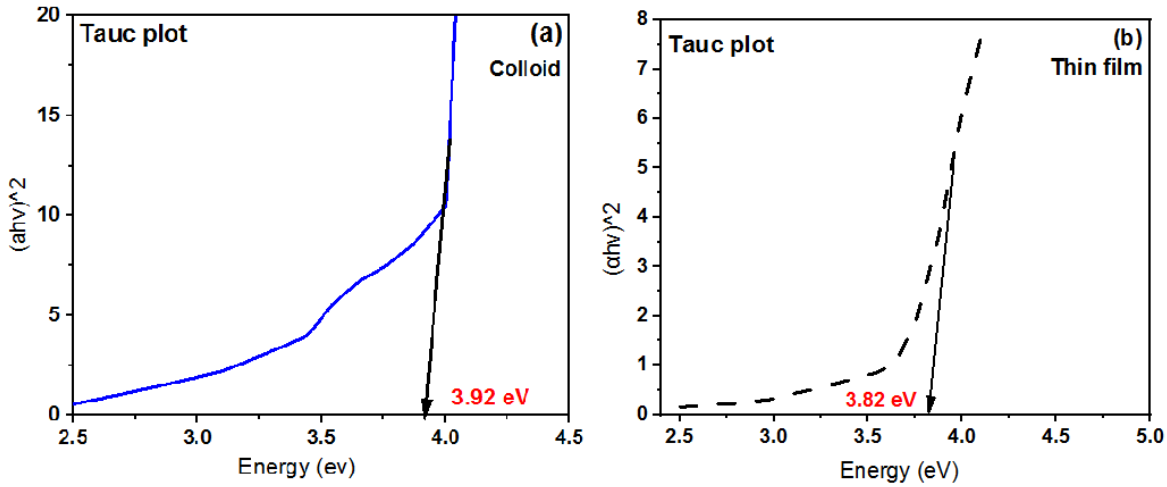

Fig. 4. shows Tauc plot for determination of bandgap utilizing $(\alpha h\nu)^2$ vs hν for ZnS sols(a) and ZnS thin film (b).

The most fundamental property of nanocrystalline semiconductors is the bandgap between the full valence band and the empty conduction band. The excitations of electrons across the band gap are allowed, producing an increase in the absorption at the wavelength corresponding to the bandgap energy. Transitions across bands in semiconductor thin films depends on the absorption coefficient (α) and photon energy (hν) by the relation (Baykul and Balcioglu, 2000; Vishwakarma, K., 2013).

$$(\alpha h\nu) = k(h\nu - Eg)^m \quad (1)$$

where α=2.3026 (Absorption/Thickness), h=Planck's constant, ν=(C/λ), k is a constant and it is related to the effective masses of electron and hole, m equal 1/2 for direct bandgap and 1 for indirect bandgap. By using Eq. (1), a graph is plotted between $(\alpha h\nu)^2$ versus photon energy (hν) to obtain a straight line (as shown in Fig. 4 (a,b). The extrapolation of the straight line to the *hν* axis gives the value of the bandgap. The bandgap energies of ZnS colloid and the thin film were estimated in the range of 3.92eV and 3.82 eV respectively, which are higher than the bandgap of the bulk bandgap of ZnS (3.68eV) due to reduced dimensions of crystallites and quantum confinement. However, the particle size of ZnS colloid and film was3.7 nm and 4.2 nm respectively. The particle size calculated from the absorption spectra by the use of Brus equation (Brus, L.E., 1984, Albrasi *et al*., 2019).

$$Eg = E_{bulk+}\frac{h\pi}{2R^2\left(\frac{1}{me}+\frac{1}{mh}\right)} - 1.8e^2/\varepsilon R \quad (2)$$

In equation 2, Eg is bandgap energy of the nanoparticle, E_{bulk} is bandgap energy of the bulk of ZnS nanoparticles which is 3.68eV, h is Planck's Constant, R nanoparticles size, m_h and m_e are effective mass for electrons and hole, *e*=1.602 X 10^{-19} unit, ε is dielectric constant.

Table 1

Particle size calculating from bandgap energy

Sample	Wavelength (nm)	Band gap (eV)	Particle size (nm)
Colloid	316	3.92	3.7
Thinfilm	324	3.82	4.2

The bandgap and particle size values for colloid of ZnS and thin film of ZnS are shown in Table 1. From the table, it is clear that the band gap decreases with the increase in the particle size.

4. Conclusion

Nanocrystalline ZnS thin film was deposited at the interfacial region between the water and toluene at 60°C by wet chemical method, using zinc sulfide colloid as starting material and cysteine as capping agent. The UV-vis technique was utilized to determine the bandgap energies for ZnS colloid and thin film. The shift in the absorption position was indicated to the formation of the nanoparticles. The bandgap energies of ZnS colloid and thin-film recorded in the range of 3.92 -3.82 eV, which is higher than that of bulk ZnS, indicating the existence of quantum confinement. The particle size of the samples was calculated by the bandgap energies, which estimated from the UV absorbance spectra and found to be in the range of 3.7-4.2 nm. It is observed that there was an increase in particle size when the bandgap is decreased.

Acknowledgments

The authors are thankful to Faculty of Education for support, E.A wishes to thank Dr. Masood Akhtar, University of Manchester (UK) for his comments.

References

Akimov, Y.A., Koh, W.S., Sian, S.Y., and Ran, S.Yu. (2010)'Nanoparticle-enhanced thin-film solar cells: Metallic or dielectric nanoparticles', *Journal of Applied Physics Letters*, 96(7), pp. 073111-073113.

Akimov, Y.A. and Koh .W.S. (2010)' Resonant and nonresonant plasmonic nanoparticle enhancement for thin-film silicon solar cells', *Nanotechnology*, 21(23), pp. 235201-235206.

Achermann, M., Petruska, M.A., Kos, S., Smith, D.L., Koleske, D.D., and Klimov, V.I. (2004)'Energy-transfer pumping of semiconductor nanocrystals using an epitaxial quantum well', *Journal of Nature*, 429 (6992), pp. 642-646.

Anker, J.N., Hall, W.P., Lyandres, O., Shah, N.C., Zhao, J., Van. Duyne, R.P. (2008) 'Biosensing with plasmonic nanosensors', *Journal of Nat Mater*,**7**(6), pp. 442-453

Albrasi, E., Almabro, S., and Thomas, J.P. (2019) 'Effect of the capping agent on the optical absorption edge of copper oxide nanoparticles film', *Journal of AppliedScience*, 2(3), pp.10-16.

Agrawal, Ved. V., Kulkarni, G.U., and Rao, C.N.R. (2005)'Nature and properties of ultrathin nanocrystalline gold films formed at the organic-aqueous interface', *Journal of physical chemistry B*, 109(15), pp. 7300-7305.

Agrawal, V.V, Mahalakshmi P., Kulkarni, G.U., Rao, C.N. (2006)'Nanocrystalline Films of Au-Ag, Au-Cu, and Au-Ag-Cu Alloys Formed at the Organic-Aqueous Interface', *Langmuir*, 22(4), pp. 1846-1851.

Baykul, M.C., and Balcioglu, A. (2000) 'AFM and SEM studies of CdS thin film produced by an ultrasonic spray pyrolysis method, Journal of Microelectronic', *Engineering*, 51(52), pp. 703-713.

Brus, L.E., Ellison, J.L., Gibson, J.M. (1984) 'Size effects in the excited electronic states of small colloidal CdS crystallites', *Journal of Chemical Physics*, 80(9), pp. 4403-4464.

Burda, C. X., Chen, R., Narayanan, M.A., and El-Sayed, M.A (2005) 'Chemistry and properties of nanocrystals of different shapes', J*ournal of Chem. Rev*, 105(4), pp. 1025-1029.

Choudapura, V.H., Kapatkara, S.B. and Rajub, A.B. (2019) 'Structural and optoelectronic properties of zinc sulfide thin films synthesized by co-precipitation method', *Journal of Actachemicaiasi*, 27(2), pp. 287-302.;

Cushing, B.L., Kolesnichenko, V.L., and O'Connor, C.J. (2004) 'Recent advances in the liquid-phase syntheses of inorganic nanoparticles', *Journal of Chem. Rev*, 104(9), pp. 3893-3946.

Duan, H.W., Wang, D.Y., Kurth, D.G., Mohwald, H. (2004) 'Directing self-assembly of nanoparticles at water/oil interfaces', *Journal of Angew. Chem., Int, Ed*, 43(42), pp. 5639-5643.

Fan, D., Thomas, P. J., and O'Brien, P. (2007) 'Deposition of CdS and ZnS thin films at the water/toluene interface', *Journal of Materials Chemistry*, 17(14), pp. 1381–1386.

Gerion, D. W., Parak, J., Williams, S.C., Zanchet, D., C.M, Micheel, C.M., Alivisatos, A.P. (2002) 'Sorting Fluorescent Nanocrystals with DNA', Journal of the American Chemical Society, 124(24), pp. 7070-7074.

Hernandez-Fenollosa, M. A., Lopez, M. C., Donderis, V., Gonzalez, M. B., and Ramos-Barrado, J. R. (2008).'Role of precursors on morphology and optical properties of ZnS thin films prepared by chemical spray pyrolysis', *Journal of Thin Solid Films*, 516(7), pp. 1622–1625.

Huynh, W.U., Dittmer. J.J., and Alivisatos. A.P. (2002) 'Hybrid Nanorod-Polyme Solar Cells', *Science*, 295(5564), pp.2425-2427.

Lodahl, P., FlorisvanDriel, A., Nikolaev, I.S., Irman, A., Overgaag, K.,Vanmaekelbergh, D., Willem, L.V. (2004) 'Controlling the dynamics of spontaneous emission from quantum dots by photonic crystals', *Journal of Nature*, 430(7000), pp. 654-657.

McDonald, S.A., Konstantatos, G., Zhang, S., Cyr. P.W., Klem, E.J., Levina, L., and Sargent, E.H. (2005)'Solution-processed PbS quantum dot infrared photodetectors and photovoltaics', *Journal of Nat Mater*, 4(2) pp.138-142.

Mattoussi, H., Mauro, J.M., Goldman, E.R., Anderson, G.P., Vikram, C.S., Mikulec, F.V., Moungi, G. B.(2000) 'Self-Assembly of CdSe–ZnS Quantum Dot Bioconjugates Using an Engineered Recombinant Protein', *Journal of the American Chemistry Society*, 122(49) pp. 12142-12150.

Mezan, S.O., Abdullah, H.J., Maytham, Q.H., Alaa, N.T., Nabeel, N.H., Mohd, A.A. (2018) 'Synthesis and Characterization of Zinc Sulphide (ZnS) Thin Film Nanoparticle for Optical Properties', *Journal of Global Pharma Technology*, 10(7), pp. 369-373.

Okuyama, K.I., Lenggoro, W., Tagami, N. (1997) 'Preparation of ZnS and CdS fine particles with different particle sizes by a spray-pyrolysis method', J. Mater. Sci., 32, pp.1229-1237.

O'Brien, P., and Nomura, R.(1995)'Single-molecule precursor chemistry for the deposition of chalcogenide(S or Se)-containing compound semiconductors by MOCVD and related methods', *Jornal of Mater. Chem*, 5(11), pp. 1761-1773.

Pathan, H. M., and Lokhande, C. D. (2004) 'Deposition of metal chalcogenide thin films by successive ionic layer adsorption and reaction (SILAR) method', Journal of Bulletin of Materials Science, 27(2), pp. 85–111.

Rao, C.N.R., Müller, A., and Cheetham, A.K. (2007) 'Recent Developments and New Directions', *Nanomaterials Chemistry*, Wiley,VCH, New York.

Rao, C.N.R., Thomas .P.J., and Kulkarni, G.U. (2007) Nanocrystals: Synthesis, Properties, and Applications, Springer-Verlag, Berlin.

Rao, C.N.R., Kulkarni, G.U., Agrawal, Ved., V., Gautam, U.K., Moumita, G., Tumkurkar, Usha. (2005)'Use of the liquid-liquid interface for generating ultra-thin nanocrystalline films of metals, chalcogenides, and oxides', *Journal of Colloid and Interface Science*, 289(2), pp. 305-318.

Rahdar, A., Aliahmad, M., Asnaashari, H. (2013) 'Effect of different capping agents on the undopedZnS semiconductor nanocrystals: Synthesis and Optical and Structural characterization', *Advanced Science Letters*, 19(2), pp. 547-549.

Roy, P., Ota, J.R., Srivastava, S. K. (2006).' Crystalline ZnS thin films by chemical bath deposition method and its characterization', *Journal of Thin Solid Films*, 515(4), pp. 1912–1917.

Tiwary, C.S., Saha, S., Kumbhakar, P. and Chattopadhyay, K. (2014)'Observation of Combined Effect of Temperature and Pressure on Cubic to Hexagonal Phase Transformation in ZnS at the Nanoscale', *Journal of Crystal. Growth& Design*, 14(9), pp. 4240-4246.

Shaoqin, L., Zhiyong, Tang (2010) 'Nanoparticleassemblies for biological and chemical sensing', *Journal of Materials Chemistry*, 20(1), pp. 24-35.

Sam, S.R (2017) 'Nano-physics ZnS nanoparticles 1st printed by CSMFL,India.Stanic, V., Etsell, T.H., Pierre, A.C. (1997) Metal sulfide preparation from a sol–gel product and sulfur', *J. Mater. Chem*., 7, pp. 105-107.

Seo, K. W., Yoon, S. H., Lee, S. S., and Shim, I. I.-W. (2005) 'Preparation of ZnS thin film using Zn (dithiocarbamate)2 precursors by MOCVD method',*.Bull. Korean Chem. Soc*., 26(10), pp.1582–1584.

Senapati, U.S, Jha, D.K., Sarkar, D., Res. (2013) 'Green Synthesis and Characterization of ZnS nanoparticles', *Journal of Physical Sciences*, 1(7), pp. 1-6.

Stansfield, G., Johnston, H., Baxter, S. & Prabhakar, J.T. (2018) 'Deposition of Ag andInterface', *Journal of RSC Advances*, 8, pp. 6225-6230.

Vishwakarma, K. (2013) 'Study of Structural and Optical Properties of ZnSNanoparticles', *Asian Journal of Chemistry*, 25(201), pp. 45-47.