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Absorption spectra and band gap of thin film nanocrystalline ZnS semiconductor deposited at the water/toluene interface

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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.**

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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 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

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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).

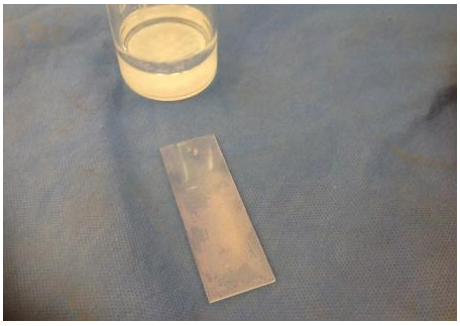

Fig. 2. Photograph shows of ZnS thin film formed at the water/toluene at 60°C.

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.

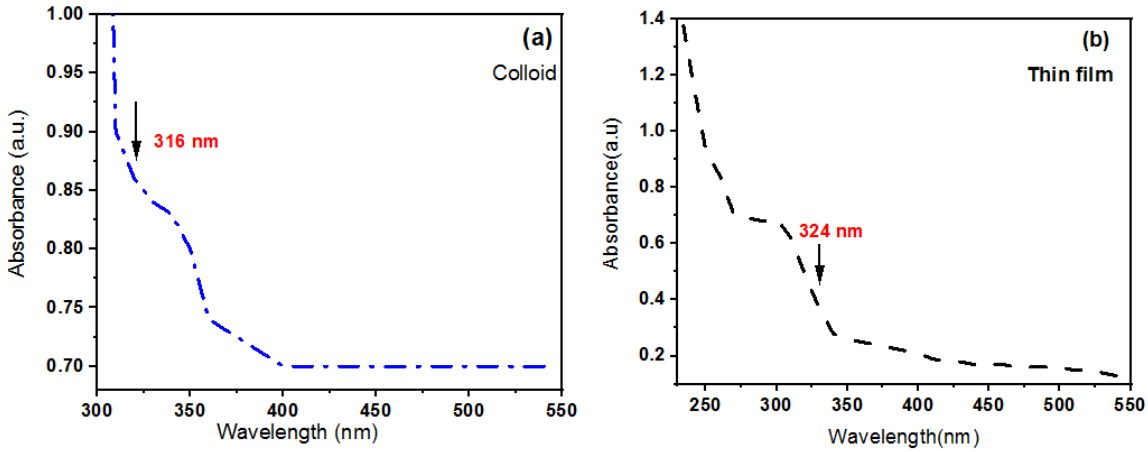

Fig. 3. Exhibits (a) the electronic absorption spectra of ZnS Sols at room temperature, (b) ZnS film at the interfacial region at 60°C.

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 Eq. (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.

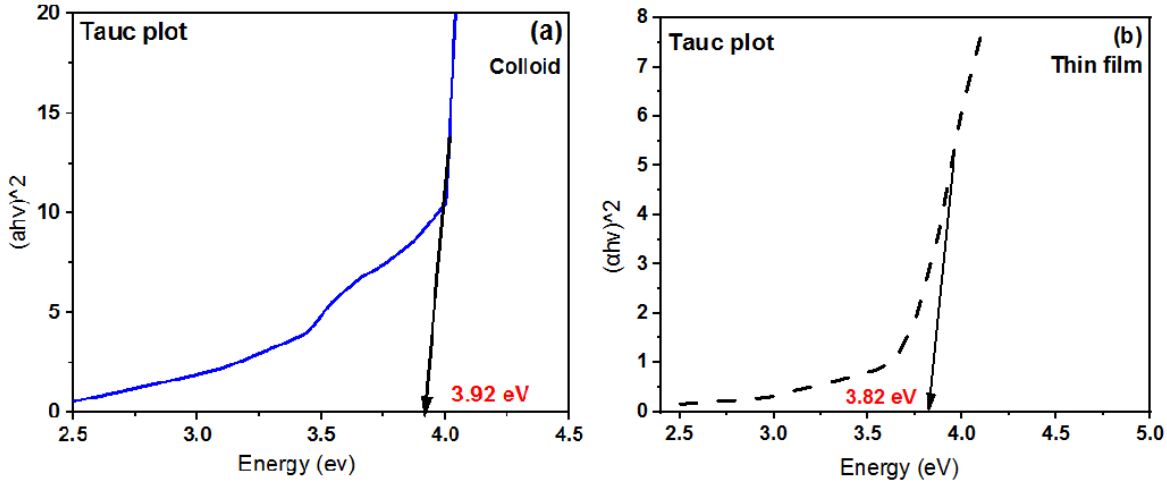

Fig. 4. Tauc plot for determination of bandgap utilizing $(\alpha h\nu)^2$ vs hν for ZnS sols(a) and ZnS thin film (b).

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.

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