

Zinc sulfide nanoparticles: processing, properties and applications: an overview

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ABSTRACT

This review is focused to understand the Zinc Sulfide nanoparticles including their structure, properties and applications. It also provides a scientific framework for advancements in Zinc Sulfide nanoparticles. This review focuses on the techniques of preparing ZnS nanoparticles with discussion on the property enhancements due to dopant incorporation as well as its application. Hence this review will be of immense use, particularly to the researchers working on Zinc Sulfide nano-materials.

KEYWORDS: Zinc Sulfide; Nanoparticles; Semiconductor; Photoluminescence; Quantum Confinement

1. INTRODUCTION

The use of nano-materials as composites are gaining importance in science and technology owing to their superior properties like mechanical, thermal, physical, chemical, electrical conductivity, optical, photoluminescence and other novel attributes Rita John et al., (2009), Pathak CS et al., (2012), Peng WQ et al., (2005). Recently, nano-composites have been introduced due to their structural characteristics like machinery parts, coatings in scratch-resistant and flame-retardant cables. Nanoparticles have been extensively investigated during the past decade due to their unique properties and potential application such as optical devices, optoelectronic devices, pharmaceutical, biomedical devices, photoconductor, solar cell and a light emitting diode material Ramrakhiani et al., (2014), Ashutosh K Shahi et al., (2011), Pathak CS et al., (2013). The magnetic nanoparticles have the therapeutics features in the nano-medicine field for the breast cancer applications. This magnetic nanoparticle also reveals the superior imaging characteristics Murali M Yallapu et al., (2012). Now a days nano-particles have strong emphasis in the technological developments. The nano-materials have sublime physical and chemical properties which is more efficient than the bulk materials. These unique properties occur when there is a change in some features like variation of size and the band gap energy Pathak CS et al., (2012). The size of the nanoparticles decreases due to the increasing band gap energy.

ZnS is one of the semiconducting materials discovered in ancient times. It is known to be a direct band gap semiconductor and has immense interest among researchers because of its potential applications, such as optical coating, photoconductors, optical sensors, phosphors, window material, dielectric filter, the field emission display and also in LEDs Xiaosheng Fang et al., (2010), Pathak CS et al., (2013). In this review we focus about the developments in ZnS nanoparticle processing techniques, properties and applications.

Background: Nano-materials are reported to have a relatively larger surface area on comparison to the same mass of material produced in a larger form. Fabrication of different kinds of nanoparticles by chemical means seems to have been well documented in the middle of the nineteenth century. When Feynman delivered his famous lecture it was already well known that the smallest viable unit of life was the cell, which could be less than a micrometer in size. His lecture shows the visionary of developing components of smaller size.

ZnS is an inorganic compound which exists in nature in dual form, Sphalerite (cubic form) and Wurtzite (hexagonal form). The material is an intrinsic semiconductor with wide band gap of about 3.54eV for cubic form of ZnS and 3.91eV for hexagonal form. These belong to II – VI semiconductors. Fig.1 (a) and Fig.1 (b) depicts the structure of zinc blende (stable form of ZnS) and wurtzite.

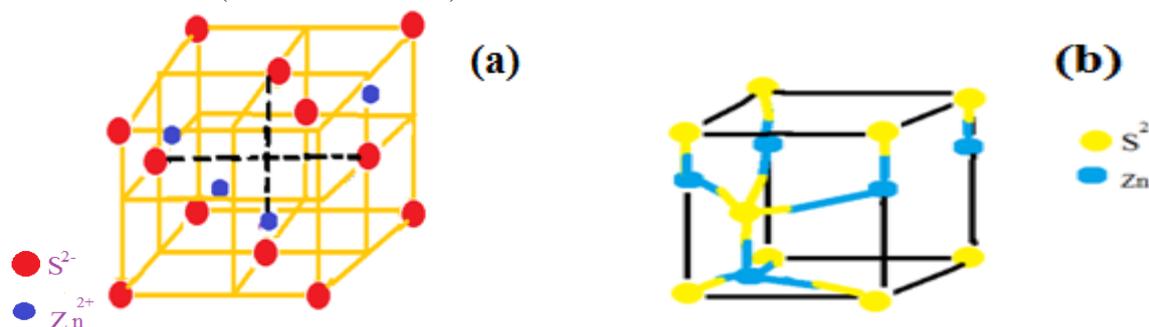


Fig.1. Structure of (a) Zinc Blende and (b) Wurtzite

Processing techniques: Sol Gel Method: Sol-gel method (Fig. 2) is alternatively called as Chemical Solution Deposition method. Sol-gel was derived from the basic fact that very small particles or molecules in the order of microns present in a solution (sols) tend to agglomerate and form a coherent network under controlled conditions. The sol gel methods involve a set of process. The first step is to prepare a homogeneous solution of highly pure

precursor(s) normally in an organic solvent which is miscible with water. The next step is to convert the solution to the form of sol by treating it with a suitable reagent, for instance for oxide ceramics treatment of water with HCl. This is followed by polycondensation to obtain 'gel'. Then shaping the resulting gel into the preferred forms like thin films, fiber, small particles and finally changing it to the desired ceramic material at temperatures (500°C). This temperature is much lower than the conventional melting temperature for the oxides. Hence this method has the advantage of low temperature synthesis Shahid M et al., (2015), Attia SM et al., (2002).

Ping Yang et al., (2002) prepared SiO₂ xerogel doped ZnS nano-crystals using sol-gel process. Bhattacharjee et al., (2003) synthesized ZnS: Mn²⁺ nano-crystallites by sol gel method. Those nanoparticles were kept in a partially densified silica gel matrix and its size in the range of 2-3 nm.

Mechanochemical Method: In mechanochemical reaction method (Fig. 3), the material is crushed by means of a strong mechanical force and this results in the formation of a different structure. Typical planetary ball mill machine adopting mechanochemical process for material crushing is currently in use. Grinding is performed by revolving continuously the large surface and consequently rotating the containers. The centrifugal speed of the plate and the planetary (rotation) speed of the container can be adjusted independently. For this process of grinding, collision of balls plays a significant role in the transfer of to the raw materials. On reception of energy by the crystallites rupturing happens. This resulted in diminishing of the particle size and an enhancement of surface area and surface energy. Such a collision effect can initiate detectable changes in the structure and may even result in chemical reactions materials, called as mechanochemical reactions Hao WU et al., (2012). For producing large scale materials in short duration of time particularly for industrial needs, the mechanochemical method can be employed.

Pathak et al., (2012) synthesized ZnS nanoparticles by the ball milling method using Zn (CH₃COO) and Na₂S as initial starting components. The size of ZnS nanoparticles is approximately 2 nm and optical band gap is about 4.71-5.17eV. Their report from XRD has proven that the ZnS material has cubic structure. Pathak et al., (2013) prepared ZnS nanoparticles using mechanochemical route by Zinc acetate and Sodium sulphide as precursors. The resulted ZnS nanoparticles size ranges between 4-7 nm and the optical band gap 4.04-4.6 eV. The composition of ZnS nanoparticles was confirmed by EDAX spectrum analysis. The synthesized ZnS nanoparticles were cubic phase structure which is same of the standard cubic ZnS. Using mechanochemical method Jianfeng Chen et al., (2004) prepared ZnS nanoparticles under the help of rotating packed bed reactor (RPBR). They used Zn (NO₃)₂ solutions along with H₂S gas are the precursors. As a result the obtained nanosized ZnS has much better absorption capacity for light of 200-330 nm wavelengths. They found ZnS has a sphalerite crystal phase.

Chemical Precipitation Method: The Chemical Precipitation (Fig. 4) involves precipitation of a solid substance which is separable from a solution, by either changing the form of the substance into a less soluble else insoluble one or diminishing the solubility of the substance by changing the composition of the solvent. Precipitation is frequently employed to remove various metal ions from the solvent.

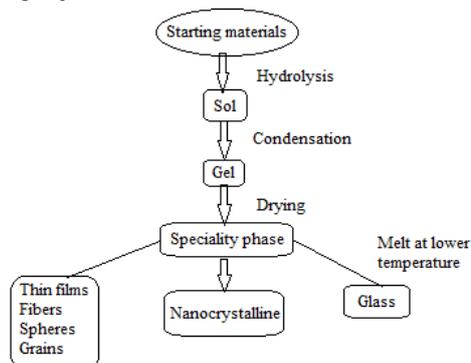


Fig.2.Flow Chart for Sol Gel Process

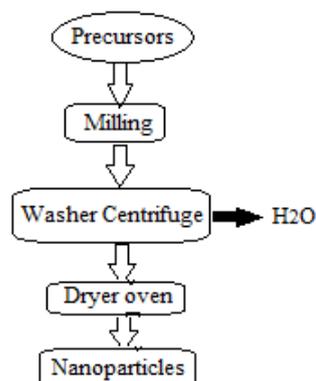


Fig.3.Flow Chart for Mechanochemical Process

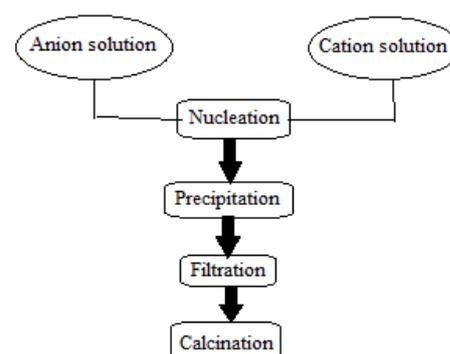


Fig.4.Flow Chart for Chemical Precipitation Process

Ashutosh K. Shahi et al. (2011) reported the preparation of ZnS small sized particles using chemical precipitation by changing the concentration of cationic surfactant N-cetyl-N, N, trimethyl ammonium bromide. This has resulted in small size (2-5nm) Zinc Sulfide nanoparticles. Using chemical precipitation method, G. Murugadoss (2012) successfully synthesized un doped, different concentrations of Cu (0.25%–1.25%)-doped and surfactant-capped ZnS: Cu²⁺ nanoparticles. This resulted in nanoparticles of pure cubic crystal structures and the estimated sizes of the uncapped and surfactant-capped nanoparticles were in the range of 3.2–5.3 nm.

Simple hydrothermal Method: Hydrothermal method (Fig.5) involves the production of inorganic nano-crystalline Materials. In this method the precursor directly reacted and allowed to produce any material without the presence of any other agents. Mostly this method is used for the inorganic substance which is soluble in water at the particular temperature and pressure. Consequently the required material can be obtained from the fluid. The water plays a vital

role for the transformation of precursor material. This method produces large good quality nano-materials O. Schaf et al., (2002).

M. Jayalakshmi et al., (2005) prepared ZnS nanoparticles using simple hydrothermal method from $Zn(NO_3)_2$ and C_2H_5NS in liquid solutions. It has the size of 15-30 nm. Its cubic structure is confirmed by TEM analysis and formation of ZnS nanoparticles is confirmed from XRD studies. By this method, one can synthesize cubic phase of sphalerite and hexagonal phase of wurtzite and cubic form of ZnS with pure phase by changing the S/Zn mole ratios M. Jayalakshmi et al. (2005).

Solid State Reaction Method: The method of solid-state reaction (Fig. 6) is one among the most commonly used method for synthesizing polycrystalline solids starting with a combination of solid materials. Usually solids are less reactive at room temperature over a period of time but on heating to much higher temperatures of 1000 to 1500 °C, reaction between the solids occurs at an appreciable rate. The rate of reaction and feasibility of formation in this method depends on the reaction conditions, surface area of the solids, properties of the reactants, their reactivity and the thermodynamic free energy change connected with the reaction.

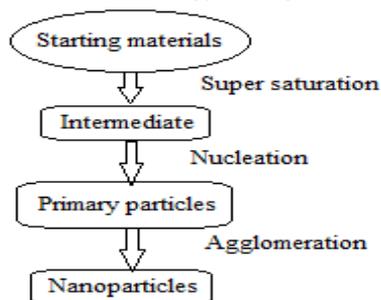


Fig.5.Flow chart for hydrothermal process

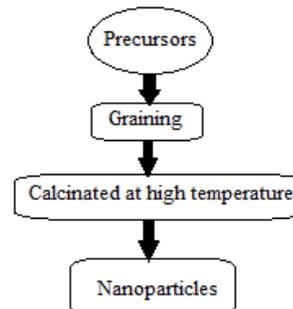


Fig.6.Flow Chart for Solid State Reaction Process

Rita John et al., (2009) prepared ZnS nanoparticles using method solid state reaction from $Zn(CH_3COO)_2$, H_2O and Na_2S as initial materials. The resulted particles have size of 11nm. The synthesized phase has cubic structure. Using FTIR spectroscopy the various vibrational modes are studied. Hao-Ying Lu et al., (2004) synthesized ZnS nanoparticles using method of solid-state reaction from $Zn(CH_3COO)_2$ and thioacetamide as the starting materials. The final nanoparticles have small in size of 3.6nm under the temperature of 100°C. Tao-Yu Zhou et al., prepared the ZnS nanowires by using solid-state reaction method at room temperature. The resulted nanoparticle is cubic in phase and is confirmed through XRD results. TEM image reveals the average size of prepared ZnS nanowires have diameters of 45 nm and up to 10µm of long. By solid state reaction method Wang et al. (2000) prepared ZnS nanoparticles using zinc acetate and thioacetamide as precursors. The resulted particles are determined to have pure zinc-blende in structure (cubic phase). The TEM analysis revealed that the ZnS nanoparticles were having size in the order of 40nm. Liping Wang et al. (2010) synthesised Eu^{3+} and Mn^{2+} doped ZnS nanoparticles using method of solid-state reaction at very low temperature. The resulted doped zinc sulfide nanoparticles have zinc-blende (cubic phase) structure. Synthesized high pure ZnS nanoparticles by dry method with $Zn(CH_3COO)_2$, H_2O and thiourea as the initial components under air atmosphere. The resulted ZnS nanoparticles were found to have third-order optical nonlinearity which is measured with the help of Z-scan technique. The prepared ZnS nanoparticles reveals high purity of single-phase sphalerite (cubic) crystal structure from XRD analysis. From optical absorption spectra, the zinc sulfide nanoparticles exhibits well quantum confinement effect Vijai Anand et al., (2015).

Wet Chemical Method: Wet chemical synthesis (Fig.7) allows the preparation of inorganic particles, oxides or metals, from the molten solution of the precursors. This method eventually helps in attaining multi component phases, with controlled size and shape, high chemico-physical reactivity and very high purity control. The processes are based on the hydrolysis (for oxides) or on the reduction (for metals), in water or in organic solvents, of metal precursors, caused by pH changes or by the addition of reducing agents.

By Wet chemical method copper doped zinc sulphide nanoparticles were prepared with zinc acetate and copper acetate as precursor Dongyeon Son et al., (2007). Their results confirmed that the ZnS:Cu material has cubic structure. The average size of the prepared ZnS:Cu material is calculated as 3.5 nm Dongyeon Son et al., (2007). Table 1 shows the various sized Zinc sulphide nanoparticles.

Properties: Ping Yang et al., (2003) reported that the fluorescence ability of the silica xerogel enhanced by ZnS nanocrystals is 3 times that of without doped sample. They observed from TEM analysis, while on increasing the impurity ratio of ZnS the size of nanocrystallites also increases. Pathak et al., (2013) reported the significant release of blue light under UV excitation of 280nm. From the PL spectra they observed that with increase of temperature, a narrow emission band was seen and it represents the zinc sulfide nanoparticles have good crystalline structure Pathak CS et al., (2013). Bochev et al., (2013) pointed out that an increase the amount of precursor's concentration but doesnot change the size of nanoparticles. Their observations from UV-vis spectra analysis showed that an increase in the precursor's concentration resulted in an increase in the absorbance value. Rita John et al., (2009) observed from

UV spectrum that the absorption occurs at about 400 nm and the band gap was found to be 3.62eV, which is high compared with sphalerite ZnS (3.54eV). From the PL studies, they observed blue emission band centered at 440 nm. W.Q. Peng et al., (2003) observed from PL studies there is two blue luminescence peaks (centered at 411 nm and 455 nm) occurs that indicates the undoped ZnS particles in nano size and a another peak of 500 nm for the copper doped zinc sulfide nanoparticles. Their report states that as the concentration of Cu^{2+} raises the intensity of photoluminescence lowers and this causes due to the CuS compound formation. From the UV-visible spectra, the absorption of Cu doped ZnS nanoparticles occurs at 316 nm. Also the Cu^{2+} ions incorporated ZnS showed no change in the diameter of nano crystalline particles. The optical band gap energy of ZnS:Cu nano size particles is 3.92 eV which is greater compared with bulk ZnS. For this wide band gap can be attributed to the quantum confinement effect of the ZnS: Cu nanostructures Peng et al., (2003). Pathak et al., (2013) observed from SEM analysis of ZnS prepared by mechanochemical route that at low temperatures (100°C) agglomeration of the particle occurred and on heat treatment at high temperatures resulted in spherical shaped ZnS nanoparticles. Bhattacharjee et al. (2002) observed from PL spectrum, the prepared ZnS: Mn^{2+} nanoparticles have broadened emission of blue peak (420 nm) at room temperature and yellow - orange peak (590 nm) related with Mn^{2+} . Wang et al., (2000) found that the particle size increases due to the increasing of temperature. In photoluminescence emission spectrum they observed blue shift. Liping Wang et al., (2010) stated the size of the obtained doped ZnS nanoparticles varies and that it is particularly depending on the doping concentration as well as the temperature. They also observed the ZnS nanoparticles have enhanced luminescence from UV analysis. Vijai Anand et al., (2015) reported that the prepared ZnS nanoparticles have negative nonlinearity which is confirmed by nonlinear optical (NLO). From PL studies they observed that the excitation wavelength (310 nm) of the synthesized ZnS nanoparticles had a weak and broaden peak at 355 nm while a strong and blue-green emission peak occurred between 400-560 nm.

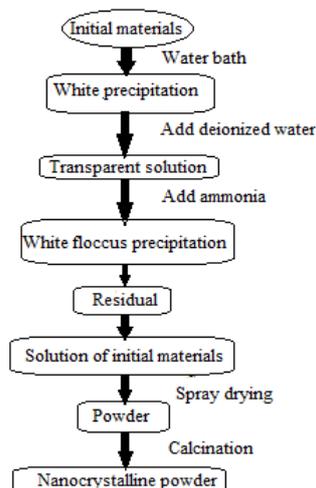


Fig.7.Flow Chart for Wet Chemical Process

Table.1.Various sized Zinc Sulphide Nanoparticles Measurement

Name of the Compound	Method	Dopant/modifier/ Precursors	Particle Size (nm)
ZnS	Sol Gel Method	SiO_2 Xerogel	2.4
		Mn^{2+}	2-3
	Chemical Precipitation Method	N- Cetyl-N,N,Trimethyl, Ammonium Bromide	2 -5
		Cu^{2+}	3.2- 5.3
	Simple Hydrothermal Method	$\text{Zn}(\text{NO}_3)_2 + \text{CH}_4\text{N}_2\text{S}$	15 - 30
	Dry Method	$\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O} + \text{Na}_2\text{S}$	11
		$\text{Zn}(\text{CH}_3\text{COO})_2 + \text{C}_2\text{H}_5\text{NS}$	3.6
		$\text{Zn}(\text{CH}_3\text{COO})_2 + \text{C}_2\text{H}_5\text{NS}$	40
Wet Chemical Method	Cu (Dopant) $\text{Zn}(\text{CH}_3\text{COO})_2 + \text{Cu}(\text{CH}_3\text{COO})_2$	3.5	
Liquid-Solid-Solution Method	Mn(dopant) $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O} + \text{CH}_3\text{CSNH}_2$	7.3 ± 0.7	
Mechanochemical Method	$\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O} + \text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$	4 - 7	

Applications: B. Bochev et al., (2013) reported the preparation of water-dispersible nanoparticles, which is beneficial for researchers who are achieving suitable methods for the preparation of nanoparticles which is dissolving in water. Murugadoss G et al., (2014), The nanoparticles of ZnS doped with Cu²⁺ creates a bio-organic interface with bio-compatible inorganic material as in nano size fluorescent probes which has possible applications in medical fields, such as drug delivery, pharmaceutical, biological and, ultra-sensitive disease detection and labeling in biological cells and optoelectronic devices Pathak CS et al., (2013) and Murugadoss (2011). Fine ZnS powder acts as a photocatalyst, which produces hydrogen gas from water upon illumination. During synthesis of ZnS nanoparticles, the colour changes from white-yellowish into a brown powder, and it improves the photocatalytic activity through enhanced light absorption Wang et al., (2015). The enhanced functions of nanoparticles are obtained by reducing the characteristic dimensions, thereby they have an extended range of accessibility. For example, organic polymer matrices incorporating carbon nano tubes can be light and very strong, or transparent and electrically conducting. Incorporation of nanostructures like conducting graphene is key to the development of devices in science and technology. Jayalakshmi et al., (2002) reported, the ZnS nanoparticles can deliver high rate of power during the short time. They have reported that the material performs as good capacitor electrodes. Murali M. Yallapu et al., (2012) found that the magnetic nanoparticles have the therapeutics features in the nanomedicine field for the breast cancer applications.

2. CONCLUSION AND FUTURE OUTLOOK

This review presents an in depth review about ZnS its unique properties and its major uses. More focus is provided for the luminescence properties, physical and chemical properties prepared using variety of techniques. The light emitting property tuned using several impurities like Mn-doped ZnS nano-belts, Cu-doped ZnS nano-rods, and also Mn/Cd co-doped-ZnS nanostructures. The structural morphology and sizes play a distinct role in electronic applications. The fruitful review underwent shows that low dimensional ZnS has become one among the favoured research activity. Although this area has shown many achievements, several key issues has also emerged that should be overcome for the purpose of practical applications. The survey reveals that only limited procedures exists for high temperature synthesis of ZnS nanostructures, which shows quantum confinement effects. Finally, one more vital challenge exists to stabilize nanoparticles in liquids without employing capping agents.

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