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A Review on Zinc Sulphide Nanostructure, Synthesis and Various Applications

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Abstract: ***Zinc Sulfide (ZnS) thin film has attracted increasing attention due to their potential applications in the new generation of nano-electronics and opto-electronics devices. The physical and chemical properties of ZnS have outstanding quality for different applications. Moreover, ZnS doped with various elements are creating a new era for both academic research and industrial applications. So, the optical properties of modified ZnS thin film will help us to find a suitable doping element for convenient deposition which may enhance the conductance and transmitting properties of the film. In this paper the synthesis of zinc sulfide nanoparticles by different routes has been discussed. The emergence of nanotechnology and the synthesis of nanomaterials have revolutionized the field of science and technology. ZnS tends to show the most promising nanoscale morphologies among the inorganic semiconductors thus possessing versatile novel properties and applications. These applications include their use in Field Emitting Diodes (FET), electroluminescence, sensors (UV-light sensors, gas sensors, biosensors), flat panel displays. This article begins with the brief introduction to ZnS its structure, description of physical, chemical and electronic properties. Further followed by the recent experiments conducted in order to improve its nanoscale properties and thus idealizing its applications***

Keywords: Zinc sulphide; ZnS Properties, Electroluminescence; Sensors

1. Introduction

The emergence of nanotechnology is often credited to renowned Physicist Richard Feynman's talk, entitled "There's Plenty of Room at the Bottom: Invitation to Enter a New Field of Physics" held at an American Physical Society meeting at the California Institute of Technology in 1959. A nanometer is a one billionth of a meter i.e. 10-9 m. The nanomaterials exhibit distinctive physical properties as compared to the bulk. The size dependent properties at this scale make nanomaterials capable of enhancing the performance and shelf life of number of products in the industrial sector [1]. The rapid growth of nanotechnology during the last decade has spawned an increasing interest in the search of methods to control the properties of nanoscale materials. Quantum size effects become large in materials with sizes in the range of the nanometre, which makes the properties of these materials dependent to a great extent on their size and structure [2].Nanomaterials and nanostructures play the important role to increase the device functionalities of nanoscience in the fields of energy sources, environments, and health [3,4] . Nanomaterials are increasingly gaining the attention of not only the scientific community but also the public due to their unique properties, which lead to new and exciting applications [5] [6] [7] . For the last few years the investigation has been focused on the preparation and characterization of II-VI semiconductor nanoparticles for applications in biological field as molecular probes or bio labels [8] and also have attracted much attention in photo and electroluminescence properties because of their size-dependent (which is tunable) and have promising optoelectronic applications [9] . Among these families, a nontoxic semiconductor zinc sulfide (ZnS) is one of the most important and typical crystalline phosphors for both applications and basic research. In particular, doped-ZnS phosphors have been investigated extensively, because ZnS, a good host material, is an important versatile and luminescent material with a wide band gap (3.6 eV). The optical properties of various ZnS doped nanocrystals and the potential applications of these luminescent materials have been reported by different groups [10]. ZnS nanoparticles in their doped and co-doped form with transition and inner transition metals have received much attention as a class of particularly luminescent materials. Different metal ions such as Cu, Ni, Co, Fe, Mn, Pb, Co, Cd, Eu, and Sm etc. doped with ZnS have been studied by many researchers because of their extensive photoluminescence (PL) properties [11] . Generally, ZnS doped with these metal ions provides new opportunities as full-color luminescence in the UV-visible region which used for various applications as well as research purposes. Now as traditionally shown remarkable fundamental properties versatility, it has a promise for novel diverse applications, including light-emitting diodes (LEDs), electroluminescence, flat panel displays, infrared windows, sensors, lasers, and biodevices, etc. Its atomic structure and chemical properties are comparable to more popular and widely known ZnO. However, certain properties pertaining to ZnS are unique and advantageous compared to ZnO. To name a few, ZnS has a larger bandgap of 3.68 eV and 3.91 eV for cubic zincblende (ZB) and hexagonal wurtzite (WZ) ZnS, respectively, than ZnO (3.4 eV) and therefore it is more suitable for visible-blind ultraviolet (UV)-light based devices such as sensors/photodetectors [12]. On the other hand, ZnS is traditionally the most suitable candidate for electroluminescence devices [13]. Beside this, ZnS is considered one of the best materials for the CIGS solar cells among possible alternative buffer layers. In comparison with CdS, the advantages of ZnS include its non-toxic and environmentally safe handling as well as its ability to provide better lattice matching to CIGS absorbers having energy band gaps in the range of 1.3 to 1.5 eV compared with CdS and having a wider energy band gap compared with CdS, which transmits even higher energy photons and increases the light absorption in the absorber layer [14] . Recently, ZnS scintillation detectors have even been used in the potential detection of dark electric matter objects (DAEMONS) [15]. These objects can catalyze the fusion of light nuclei, suggesting new ways for solving the problem of deficiency of solar neutrinos and of solar energetic as a whole. The specific aim of this review work is to find novel potential applications of ZnS and also to compare the properties of ZnS doping with various elements. This review article contains four doping elements for ZnS thin film Cu, Ni, Co & Fe as descending order of atomic number matching with Zn's atomic number along with possible comparisons among them. Moreover, potential applications of ZnS are also added based on above-doing elements as well as other elements.

Zinc Sulphide (ZnS)

ZnS has been widely studied as nanomaterials. Traditionally, ZnS has also been studied both in bulk and thin film form for a very long time. ZnS is one of the first semiconductors discovered that has shown the remarkable properties that can be exploited for versatile applications including field emitters, electroluminescence, electro catalyst, biosensors. Compared to bulk ZnS, nano ZnS possess anomalous physical and chemical properties such as: enhanced surface to volume ratio, the quantum size effect, surface and volume effect and macroscopic quantum tunneling effect, more optical absorption, chemical activity and thermal resistance, catalysis, and the low melting point. It is an important II-VI group semiconductor compound having a wide and direct band gap of 3.72 eV for the cubic phase [16] and 3.77 eV for the hexagonal-wurtzit phase [17] at room temperature. It has relatively large (~ 40 meV) exciton binding energy. ZnS diplays a high refractive index of ~2.2 and having high transmittance of light in the visible region of the spectrum [18]. ZnS is applicable for a variety of applications such as electroluminescence devices, solar cells and many other optoelectronic devices. Zns has a low excition Bohr radius (2.5 nm) that makes its nanoparticles interesting as small bimolecular probes for fluorescence and laser scanning microscopy [19].

Most of works on ZnS low dimensional system reported ZnS nanostructured like nanoparticles, nanotube, nanowire, nanosheets, nanorods, nanobelts etc. Recently, optical wave confining and lasing has demonstrated in Zns nanoribbons [20]. Doped ZnS nanocrystals have changed properties, especially, the transition matellic ions co-activated Zns nanoparticles form of a new class of luminescence material. Doping of ZnS nanoparticles by transition metal ions eg Mn^{2+}, Cu^{2+} and rare earth ions eg Eu^{2+} have been successfully achieved by different worker. Embedding the ZnS nanoparticles in Zeolite, Plymer, glasses, silica etc. gives the possibility to obtain materials with desired properties owing to control of the nanoparticle size. ZnS is also currently used as a shell or capping layer in core/shell nanoparticles such as CdSe/Zns core/shell structures [21].

Crystal Structure of Zinc Sulphide (ZnS)

The nanostructures can be realized through different types of structures as well as through different materials. In its bulk form, ZnS is typically found in the zinc blend crystal structure at room temperature [22]. The zinc blend structure is cubic, with four sulfur anions per unit cell located at the corners and centers of each face and with four zinc cations situated in half of the tetrahedral sites (the ¼,¼, ¼ positions). At elevated temperatures, bulk ZnS can undergo a phase transformation from the cubic zinc blend structure to a hexagonal crystal structure known as the wurtzite structure. This transformation has been shown to occur at 102^{0o} C. The zinc blend and wurtzite structures are very similar. The stacking sequence of the close-packed planes of zinc blend (the (111) planes) is represented by the ABCABCABCABC repeating pattern. However, if the close-packed planes stack themselves in the ABABABABAB repeating pattern, they would form the (0001) planes of the wurtzite structure. Both the zinc blend and the wurtzite structure of ZnS are shown in Fig.1

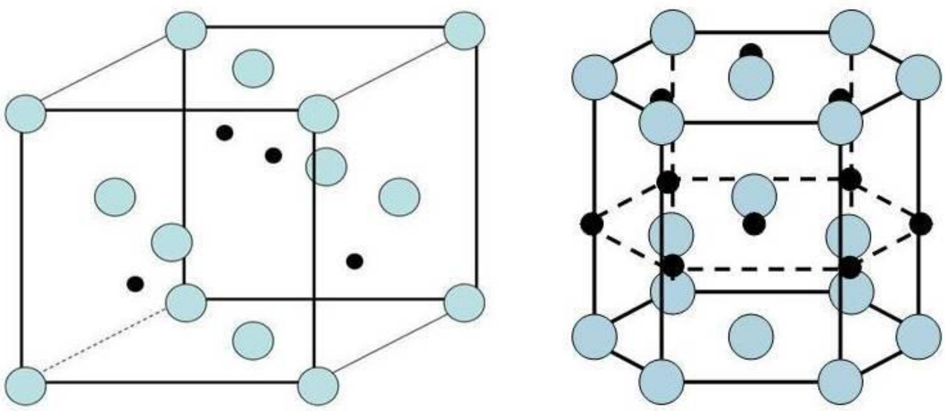

Figure 1: The zinc blende (left) and wurtzite (right) crystal structures of ZnS

The wurtzite structure has a hexagonal unit cell (space group P63mc). The structure of wurtzite ZnS can be described as a number of alternating planes composed of tetrahedrally coordinated S^{2-} and Zn^{2+} ions, stacked alternatively along the c-axis. The tetrahedral coordination in ZnS results in non-central symmetric structure and piezoelectricity. Another important characteristic of ZnS is the polar surfaces. The most common polar surface is the basal plane. The oppositely charged ions produce positively charged Zn-(0001) and negatively charged S-(000-1) polar surfaces, resulting in a normal dipole moment and spontaneous polarization along the c-axis as well as a divergence in surface energy.

Synthesis Overview

Ghosh et al. synthesized Polyvinyl Pyrrolidone (PVP) encapsulated Zinc Sulphide (ZnS) nanoparticles by adding measured amount of zinc acetate, thiourea and PVP into N, N- Dimethyl Formamide (DMF) medium with consistent stirring at 150 rpm. The resulted TEM image of ZnS NPs explained the effect of capping on size separation. It exhibited that PVP capped ZnS nanoparticles were mono dispersed in nature. Their size ranging within 2-3 nm matches with of XRD results. Whereas uncapped nanoparticles on the other hand were aggregated and were larger in sizes than capped ones. This explains the use of PVP as capping agent. Also Blue shift in absorption edge as compared to bulk ZnS clearly explained the quantum confinement effect within ZnS nanoparticles [23]. Gilbert et al. combined real space Pair Distribution Function (PDF) analysis of nanoparticle structure with the particle size analysis (zetasizer) and FTIR to point out that the nature of surface solventor ligand interactions will have an effect on the interior crystallinity of nanoparticles. The availability of particles with a variety of crystallinity provides a model system during which it's possible to see the interior disorder effects of nanoparticle, where properties like mechanical stiffness and fluorescent quantum yield are affected. PDF analysis showed that samples of ZnS nanoparticle with similar mean diameters (3.2-3.6 nm) however synthesized and treated differently possess a dramatic range of interior disorder [24]. Ram Kripal et al., prepared ZnS: Mn^{+2} by co-precipitation method and conducted their photo luminescent and photoconductivity properties. UV- visible spectra shows blue shift as compared to bulk counterpart. PL spectra show orange emission that varies with Mn^{+2} concentrations. The XRD studies estimated the size of nanoparticles to be around 2-4 nm. The TEM images overestimates the larger nanoparicle size due to drying step in sample preparation [25]. Somayeh Nazerdeylami et al. synthesized ZnS: Mn^{+2} nanoparticles capped with PVP in aqueous solution by chemical method. Prepared samples were characterized by using UV-Visible spectroscopy, XRD and PL studies. The UV data reveals that the synthesized nanoparticles show absorption near 292 nm and also that the concentration of Mn does not alter the bang gap of nanoparticles. XRD studies show that the average particle size is 2 nm and ZnS nanoparticles cubic structure. PL studies performed at room temperature show the orange-red emission at 594 nm and its intensity increases with increase in Mn^{+2} ion concentration [26]. Manoj et al. reported the study of energy transfer mechanism using different capping agents to intrinsic luminescent vacancy centers of ZnS. Co-precipitation method was used to synthesize nanoparticles of capped and uncapped ZnS. Sterically stabilized NPs were obtained using organic polymers: poly vinyl pyrrolidone, thioglycerol and 2-mercaptoethanol. TEM observation revealed that Monodispersed NPs were observed for both capped and uncapped ZnS nanopowders. Though, tendency of forming nanorod like structures existed for nanopowders of uncapped ZnS. X-ray diffraction pattern gave the size in between 1.95-2.20 nm for capped nanostructures and 2.2 nm for uncapped nanostructures. Emission intensity and Band gap were observed to be increased on addition of different capping agents in comparison to uncapped ZnS NPs. Overall result revealed that Capped ZnS NPs showed more pronounced energy transfer from capping layer to photoluminescent [27].

Potential Applications of ZnS

Zinc Sulphide has numerous applications. Among them consideration is used as recent progress on the improvement of the properties of ZnS for finding novel potential applications are included below. Such applications are various ZnS nanostructures as field emitters, field effect transistors (FETs), Electroluminescence devices, Solar cells, UV-light and chemical sensors, biosensor, Fuel Cell and Catalytic activities etc.

Field Emission (FE)

Field-emission (FE) (also known as electron field-emission) is an emission of electron-induced by external electromagnetic fields. FE can take place from solid and liquid surfaces, or individual atoms into a vacuum or open air, or result from the promotion of electrons from the valence to the conduction band in semiconductors.

FE phenomena mostly studied at room temperature and are barely temperature dependent. The determining factors for the emission current could be the work function of the emitting materials, the local electric field, the distance between a sample and the anode, and the tip geometry, the work function of an emitter surface plays a primary role in the emission current.

Field Effect Transistors (FETs)

ZnS/SiO_2 core/shell nanocables are synthesized by a vapor/liquid/solid growth method to fabricate a FETs nanodevice. This device immersed in the liquid for biological and chemical sensing, by monitoring the electrical conductance during protein or chemical additions. Protein, such as bovine serum albumin (BSA) has a strong affinity to silica surface, which makes it possible to utilize the charged BSA as a gate. The nanocable-based transistor was immersed in a PB solution with bovine serum albumin BSA 0.0005 g/L and its electrical conductance was decreased while proteins were added. The conductance was decreased upon stepwise exposure to BSA (0.0005 to 0.005 g/L), strongly suggesting that adsorption of BSA on the surface of the nanocable is responsible for the observed conductance change which used for real-time BSA protein detection. Since the nanocable is n-type, so the conductance of the device decreases when BSA is added to it. The conductance of the device, on the other hand, was found to increase when a positively charged protein was added [28].

Electroluminescence

Amongst various useful properties of ZnS, EL deserves a special mention, because ZnS is considered to be one of the best semiconducting functional materials for EL devices. EL is a phenomenon in which a material emits light in response to an electric current passed through it. This is one of the few instances in which a direct conversion of electric energy into visible light takes place without the generation of heat (incandescence), chemical reaction (chemiluminescence), or a mechanical action (mechanoluminescence). It was observed that if ZnS slightly doped with Cu suspended in an insulator and an intense alternating electric field was applied with capacitor like electrodes, visible light was emitted. The reason is when a sufficiently high voltage is applied across the electrodes, electrons that are trapped at between the interfaces layers are injected into the conduction band where they are accelerated by the field and may create excitation at the luminescent dopant centres by impact excitation and ionization mechanisms. This has led to a surge in research activities of EL properties of ZnS, which were mostly undertaken on single-crystals and powder samples [29]. The light output of thin-film electroluminescent displays has been very reliable, with little loss after tens of thousands of hours of operation.

Solar Cell

ZnS nanostructure is being intensely used in the novel solar cell such as dye-sensitized solar cells (DSSCs), quantum dot-sensitized solar cells (QDSCs), Cu (In, Ga) Se_2 (CIGS)-based thin film solar cells or organic-inorganic hybrid solar cells. Generally, ZnS nanostructure may be used as photoanode in DSSC, but the cell efficiency is too low that constitutes less than 1%. For increasing the efficiency of ZnO/ZnS core-shell, it was proposed that the ZnS layer on the ZnO nanowires suppressed the recombination of injected electrons at anode/electrolyte interface by reducing defect site.

One of the most promising thin film solar cells with high world rank efficiency is Cu (In, Ga) Se_2 (CIGS)-based thin film solar cells. The device structure of CIGS solar cell is quite complex which consist of a multilayer of metal, semiconductor, and alloy layer. Typically, CdS has been applied as a buffer layer between the absorber and front contact layer for CIGS solar cells. Because of the incompatibility deposition method and environmental unfriendly of Cadmium is a matter of concern in large-scale solar cell production. On the other hand, ZnS Buffer layer can be fabricated by a various deposition method. By using a CBD-ZnS buffer layer, the conversion efficiency of 18.1% for Cd-free CIGS thin film solar cells has achieved which controlled by O/S atomic ratio to minimize the conduction band offset at ZnS/CIGS interface and bulk recombination of those wide-gap alloys [30]

UV-Sensors

ZnS makes a promising material for fabricating optoelectronic devices. ZnS provides a novel forthcoming alternative for UV detectors due to its wide direct band gap (~3.7 eV) as compared to that of ZnO and indirect band gap of diamond (~5.5 eV). The photoresponse of ZnS nanobelts based sensors is three orders of magnitude higher upon illumination at 320nm light as compared to its response to visible light. The high spectral selectivity along with high photosensitivity and fast response time justify the use of ZnS nanobelts as a promising UV photodetector [31].

Chemical Sensors

ZnS nanocrystals have a very good photostability, continuous absorption spectra, efficient, narrow and tunable emission, which can be exploited or their application in biological imaging and single particle tracking studies. Mn+2 doped ZnS nanocrystals with amine capping layer have been fabricated and utilized for the fluorescence detection of chemicals like 2,4,6-trnitrotoluene (TNT) by quenching the strong orange Mn+2 photoluminescence [32].

Biosensors

ZnS nanoparticles have been used for label free, real time and sensitive detection of biological species. ZnS QDs are luminescent inorganic fluorophores that have the potential to overcome the functional limitations possessed by organic dyes in fluorescence labelling applications. To be a promising candidate for biosensors, the nanoparticles must have high luminescent efficiency and appropriate surface groups available in order to couple with the biomolecules. Recently CdSe/ZnS core-shell QDs conjugated with enzymes is used to sense glucose. The QDs were used as electron donors whereas enzymes were used as acceptors for oxidation/ reductions reactions involved in oxidizing glucose to gluconic acid. The newly developed QD systems possess superior design, high flexibility, low cost and good sensitivity [33, 34]

Fuel Cell

ZnS nanoparticles had catalytic activity for the decomposition of ethanol, a potentially abundant fuel for mobile electricity generation since it could be fabricated by fermentation from a broad range of organic materials [35]. Electrocatalytic conversion of ethanol in the presence of O_2 to form H_2O and CO_2 involves the transfer of 12 electrons per molecule of ethanol and proceeds via two intermediates, acetaldehyde and acetic acid. Comparison of these values with that of ZnS shows that ZnS should always be stable in the presence of ethanol against oxidation or reduction and therefore it could be a stable catalyst against ethanol oxidation. It is also important to cap ZnS nanostructures with small ligands in order to facilitate electron transfer across the surface.

Catalytic activities

ZnS is a direct band gap material with astonishing chemical stability against oxidation and hydrolysis. All these characteristics are maintained when the material is featured to nano dimensions therefore nanoparticles of ZnS are interesting entities for catalytic applications where they are exposed to violent environment. Moreover, ZnS is available in abundance in nature and is nontoxic. Therefore, they can be used as an important catalyst in environmental protection by removing organic and toxic water pollutants. ZnS have been used for the photocatalytic degradation of organic pollutants such as dyes, p-nitrophenol and halogenated benzene derivatives in waste water treatment. The photocatalytic superiority of ZnS nanoporous nanoparticles is due to the fact that due to their excellent porous structures they do not aggregate. Moreover, ZnS can be doped with Ni or Cu to adjust the photocatalytic activity under visible irradiation. ZnS nanoparticles have also been used as an electrocatalyst for the direct conversion of ethanol in fuel cells [36]

2. Conclusions

In this review article the Synthesis of ZnS nanoparticles by various methods such as chemical precipitation, sol-gel, hydrothermal, inert-gas evaporation etc have been studied. The synthesized nanoparticles were being characterized by using XRD, TEM, HRSEM, UV-Visible spectroscopy, FTIR, Zeta-sizer and PL spectroscopy. Doping of ZnS with Mn alters the band structure, optical and chemical properties and enhances the luminescence properties. These materials are nontoxic so they can be further elaborated for their application in biosensing and imaging. In report on ZnS study needed a wide variety of comparison by taking most possible elements doping on ZnS. Which demands more precise experimental data and finding them from numerous articles is a challenging criterion. However more work on turning the ZnS conductivity, bandgap, surface, and optical properties in a more controllable way can give those precise data. And this will facilitate the most conceivable development of applications for sensors, FET, LEDs, Solar cell and other optoelectronic devices based on ZnS nanostructures. Eventually, for technological applications of ZnS thin film synthesis, positioning and interconnection of these building blocks are needed for the direct integration.

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