Review Article

Research progress of ZnS nanoparticles

Abstract:

Zinc sulfide (ZnS) stands as a vital II-VI group compound semiconductor material characterized by its wide bandgap, high electron mobility, and remarkable chemical stability. Its versatility is widely recognized across domains including photocatalysis, optoelectronics, semiconductor devices, biomedical applications, and tribology. The current focal point of research centers around the precise preparation of ZnS nanoparticles with controlled particle size, uniform distribution, exceptional performance, and high stability. This review offers an overview of the various methods employed for the synthesis of ZnS nanoparticles, accompanied by an analysis of the distinguishing features of each synthesis technique. The paper also elucidates the characteristics of ZnS nanomaterials and their existing applications in diverse fields while outlining the prospects for future developments in this domain.

Key words: zinc sulfide, nanomaterials, preparation, application

1.Introduction

Nanostructured materials constitute a distinct class of materials characterized by their specific size and structure, typically within the range of 1 to 100 nanometers. Renowned for their unique properties and behavior, these materials exhibit markedly different characteristics in electronics, optics, magnetism, and mechanics due to the size effects. Leveraging their high surface-to-volume ratio and controllable dimensions, nanostructured materials find wide-ranging applications across various fields such as electronic devices, optical sensing, drug delivery, environmental remediation, nano-additives, and material reinforcement. The potential applications and ongoing scientific investigations underscore nanostructured materials as a key focal point in modern materials science and engineering.[1]。

Zinc sulfide (ZnS) stands as a pivotal member of the II-VI group, known for its significance in the realm of metal sulfide semiconductor materials. Typically manifesting as white or pale yellow powders, ZnS exhibits two prominent crystallographic phases: cubic sphalerite and hexagonal wurtzite. The sphalerite phase, characterized by its cubic crystal system, prevails as the low-temperature form, whereas the wurtzite phase, governed by a hexagonal crystal system, emerges as the high-temperature counterpart.

ZnS is distinguished by several intrinsic attributes, including polar surfaces, macroscopic quantum tunneling effects, exceptional charge transport capabilities, commendable thermal stability, and elevated electron mobility[2]. These distinctive properties render ZnS highly applicable in an array of technological domains encompassing light-emitting diodes (LEDs) [3], electroluminescence[4], displays[5], sensors[6], photocatalysis[7], tribology[8], and biomedical devices[9], to name a few.

2.Preparation methods of ZnS nanoparticles

2.1 Hydrothermal and Solvothermal Synthesis Methods

Hydrothermal synthesis, employing water as the solvent, involves the introduction of metal and sulfide precursors into a sealed pressure vessel, where they undergo a continuous reaction at elevated temperatures to yield ZnS nanoparticles. This method is characterized by its simplicity and wide applicability, with the advantage of maintaining a closed experimental environment that effectively isolates potentially

Samanta et al. [10]utilized orange juice as a capping agent to economically prepare ZnS nanospheres via a straightforward hydrothermal process. Characterization of the synthesized material revealed the presence of nanospheres, a confirmation supported by high-resolution transmission electron microscopy (HRTEM) images. Chanu et al. [11] employed amino acids, specifically l-histidine, as capping agents in a hydrothermal ZnS nanosphere synthesis, systematically investigating the impact of reaction parameters on particle size. Their experimental findings indicated the tunability of ZnS morphology and dimensions based on reaction parameters. Notably, under reaction conditions of 120°C and a reaction time of 3 hours, ZnS nanospheres with a diameter of 5 nm were obtained.In a distinct approach, Bian et al. [12]adopted a one-pot hydrothermal method to fabricate cellulose-based fluorescent materials decorated with zinc sulfide (ZnS) quantum dots on graphene. X-ray photoelectron spectroscopy (XPS) analysis was employed to determine the chemical states of Zn, S, C, O, and N in the composite material. Transmission electron microscopy (TEM) further confirmed the reduction of graphene oxide into graphene sheets, followed by the deposition of ZnS nanoparticles (10 nm) onto the graphene surface.

The solvothermal method for synthesizing ZnS nanoparticles involves the introduction of metal and sulfide precursors into an organic solvent, where they undergo a continuous reaction at high temperatures to yield ZnS nanoparticles. One of the notable advantages of this approach lies in its ability to achieve the preparation of high-purity nanoparticles with a relatively large size range.

In a study by Jiang and colleagues [13], ethanolamine (EA) was employed as an assisting agent in the solvothermal synthesis process. Zinc oxide (ZnO) and sodium thiosulfate pentahydrate ($Na_2S_2O_3·5H_2O$) were used as the starting reagents, leading to the one-step synthesis of ZnS nanorods with an average diameter of approximately 6 nanometers, possessing a fibrous zinc blende structure. The resulting ZnS nanorods exhibited a high degree of single crystallinity. Through an in-depth investigation of the raw materials, it was discerned that EA solvent played a pivotal role in governing both the phase and morphology of the ZnS nanorods.

In a parallel study, Gao and collaborators [14] utilized a mixture of ethylenediamine (En) and deionized water as the solvent in a solvothermal process, achieving the controlled synthesis of ZnS nanostructures, specifically ZnS nanowires.

By systematically exploring various synthesis parameters, including the volume ratio of En to deionized water, molar ratios of the precursor compounds, different zinc precursors, reaction temperature, and reaction time, they elucidated the mechanisms underlying the evolution of the morphological and performance characteristics of ZnS nanowires.

While the solvothermal method enables synthesis at elevated temperatures, hydrothermal synthesis is suitable for low-temperature processes. Both methods share the advantage of producing high-purity, uniformly sized ZnS nanoparticles.However, the disadvantages of the hydrothermal method are that it limits the selection of reactants, it is difficult to precisely control the reaction conditions, and it is inconvenient to operate for a long time.The disadvantages of the solvothermal method are the difficulty of solvent recovery, the high temperature that can lead to side reactions, and the high demand for test equipment and energy. Furthermore, these techniques allow precise control over the external morphology and chemical properties of the resulting crystals. Both hydrothermal and solvothermal methods find extensive applicability, enabling the synthesis of diverse nanomaterials, including metal oxides, semiconductors, and organic crystals. Consequently, these methods hold broad relevance in the fields of materials science and nanotechnology.

2.2 Co-Precipitation Method

The co-precipitation method involves the mixing of solutions containing zinc salts and sulfur precursor compounds, followed by adjustments to experimental conditions such as pH, temperature, and stirring rate. This enables the reaction between sulfur ions and zinc ions in the solution, leading to the formation of ZnS nanoparticles.

n a study conducted by Iranmanesh and colleagues [15], nanoscale ZnS crystals were prepared using the co-precipitation method with zinc acetate dihydrate ($Zn(Ace)_2 \cdot 2H_2O$), sodium sulfide (Na_2S), and ethylenediaminetetraacetic acid (EDTA) with a purity exceeding 98% as the source materials. EDTA served as a capping ligand. All reagents used were of analytical grade, and deionized water was the solvent. Specifically, 0.005 mol of $Zn(Ace)_2 \cdot 2H_2O$ and EDTA were individually dissolved in 50 ml of deionized water, with continuous stirring. The solution's pH was adjusted to 7 using the required amount of NH_4OH, resulting in a clear liquid. Subsequently, 0.1 mol of Na_2S was added to 50 ml of deionized water. The Na_2S solution was then poured into the $Zn(Ace)_2 \cdot 2H_2O$ and EDTA solution. After the reaction was complete, a white precipitate formed. The mixture was then centrifuged at 300 rpm for 30 minutes and dried in air at 110°C for 24 hours, yielding ZnS nanoparticles.

The co-precipitation method is characterized by its simplicity, ease of use, and relatively low cost. It is well-suited for large-scale production and the fabrication of ZnS nanoparticles with significant dimensions.However, it is difficult to obtain high-purity products by co-precipitation, which has high energy consumption and long reaction time

2.3Chemical Vapor Deposition Method

The preparation of ZnS nanoparticles via the chemical vapor deposition method involves introducing gaseous precursor materials (Zn source and S source) into a reaction environment, where they undergo chemical reactions at high temperatures to generate ZnS nanoparticles in the gas phase, which are subsequently deposited onto a substrate.

Zhai and colleagues[16] achieved the large-scale synthesis of ZnS nanopyramids using a straightforward two-step pressure-controlled chemical vapor deposition approach. These ZnS nanopyramids exhibit sharp tips ranging from 100 to 200 nm. This material displays robust green luminescent properties, making it a promising candidate for applications in nanoscale optoelectronic devices. Huang and his team [17] successfully synthesized single-crystal ZnS nanowires on Si (100) substrates using a simple thermal chemical vapor deposition method. These nanowires exhibit two distinct structures, namely, zinc blende and wurtzite, with diameters ranging from approximately 20 to 50 nm. The impeccable crystal structure of these nanowires underscores their potential applications in nanotechnology and nanodevice manufacturing.

The chemical vapor deposition method offers the ability to produce high-purity nanoparticles within a broad size range, making it suitable for fabricating high-quality thin films and nanowires that can be integrated into semiconductor devices.The disadvantages of chemical vapor deposition are the high requirements of the reaction equipment, the potentially dangerous test process, and the possibility that the reaction products can remain as impurities on the coating.

2.4Microemulsion Method

The microemulsion method involves the formation of a microemulsion system in an organic solvent containing a surfactant. This system is used for the synthesis of ZnS nanoparticles by introducing precursor materials of metal zinc (Zn source) and sulfur (S source) into the microemulsion and carefully adjusting reaction conditions to induce the formation of ZnS nanoparticles.

Xu and colleagues [18] employed a straightforward microemulsion approach capable of producing semiconductor ZnS nanorods and nanoparticles with diverse morphologies. In a water-in-oil (W/O) ternary microemulsion system, they successfully synthesized water-insoluble zinc sulfide nanocrystals, which were stabilized by a surfactant. The products were characterized through transmission electron microscopy (TEM), energy-dispersive X-ray spectroscopy (EDAX), and electron diffraction (ED) of individual nanorods. As the molar ratio of water to surfactant (ω0) in the solution changed, the size of the water droplets in the microemulsion also varied. This led to the formation of ZnS nanoparticles with varying morphologies, including nanorods, spheres, or ellipsoids, during the ZnS synthesis process. Furthermore, the morphologies of the products were found to be sensitive to the absolute reactant concentrations, the concentration ratio of Zn2+ to S2-, the reaction duration, and the environmental temperature.

The microemulsion method offers the advantage of controlling the particle size of the resulting nanoparticles, resulting in monodisperse nanoparticles with excellent interfacial properties.However, the preparation process of the microemulsion method is complex and requires more equipment, which increases the cost, and the use of more additives will cause drug contamination.

2.5 Sol-Gel Method

The sol-gel method involves the use of zinc salts and sulfur sources as precursors, along with additives such as complexing agents and surfactants. This method leads to the formation of sol or gel through chemical reactions, hydrolysis, and condensation processes. The resulting sol or gel is then dried, ground, and ultimately transformed into nanostructured ZnS materials.

Mandal and colleagues [19] employed the sol-gel method to synthesize ZnS nanoparticles, which were subsequently calcined at different temperatures, including 150°C, 200°C, and 250°C. The obtained ZnS nanoparticles exhibited crystallite sizes ranging from 4 to 8 nm. Similarly, Vijayan and co-workers [20] utilized the sol-gel method, employing sodium sulfide, distilled water, and zinc chloride as primary raw materials. They obtained ZnS powder through processes involving stirring, pH adjustment, precipitation, washing, heating, and annealing. The ZnS nanoparticles annealed at 200°C had a particle size of 36 nm.

The sol-gel method allows for the synthesis of ZnS particles with different sizes and shapes by adjusting reaction conditions, catering to specific application needs. This approach yields ZnS nanoparticles with high uniformity, reducing size and shape discrepancies between particles. This uniformity enhances material performance and stability and facilitates easy scalability for industrial production. The sol-gel method is applicable for various forms of ZnS, including nanoparticles, thin films, and porous materials, meeting the demands of diverse application fields.The raw materials of the sol-gel method are more expensive and harmful to health, and the reaction time is longer.

Each method possesses unique advantages and applicable scopes. The choice of an appropriate method depends on the desired properties, scale, and applications of the ZnS nanoparticles. Precise control conditions and experimental techniques are essential in nanoparticle synthesis to ensure the desired properties. Additionally, adhering to safety protocols is crucial when handling nanoparticles, considering their potential risks to human health and the environment.

3.Multi-field applications of ZnS nanoparticles

3.1Optoelectronics and Semiconductor Devices

Zinc sulfide (ZnS) nanoparticles represent a direct bandgap semiconductor with a relatively wide energy bandgap, excellent luminescent properties, and the ability to exhibit stability under specific conditions, as well as resistance to heat and chemical corrosion. These characteristics make it well-suited for semiconductor devices operating in high-temperature and harsh environmental conditions. ZnS is commonly employed in the fabrication of optoelectronic materials and semiconductor devices, including photodiodes, solar cells, fluorescent materials, and laser diodes. Furthermore, ZnS can be combined with other semiconductor materials to construct intricate electronic and optoelectronic devices, broadening its range of applications.

ZnS stands out as a promising material for optoelectronic devices, particularly in the long-wavelength ultraviolet (315–400 nm) range. ZnS nanoribbon sensors exhibit a response that is three orders of magnitude higher when exposed to 320 nm wavelength light compared to visible light. This significant difference in response is attributed to the exceptional properties of ZnS nanoribbons, including high spectral selectivity, sensitivity to light, and rapid response times, making them suitable for ultraviolet detection[21]。Li and colleagues [22] synthesized monodisperse ZnS quantum dots with an average particle size of 3.8 nm and investigated their structural, optical, and electrical properties. Experimental results revealed that ZnS quantum dots-based photodetectors exhibited a maximum responsivity of 5.8 A/W and a detection rate of 1.97×10^13 Jones when irradiated with 365 nm ultraviolet light. This demonstrates their significant potential for ultraviolet detection.Zhangand collaborators [23] conducted research on single-piece and flexible ZnS/SnO2 ultraviolet photodetectors with lateral graphene-like electrode. They employed an in-situ laser-induced graphene material as a flexible lateral electrode for ZnS/SnO2 ultraviolet photodetectors. This in-situ growth method established a robust interface between the graphene electrode and the semiconductor ZnS/SnO2, resulting in high optoelectronic performance.

3.2Photocatalysis

Zinc sulfide (ZnS) nanoparticles exhibit remarkable photocatalytic activity, encompassing the degradation of organic pollutants, photocatalytic water splitting for hydrogen (H_2) generation, photoreduction of halobenzene derivatives, and photoreduction of carbon dioxide (CO_2).

Chang and colleagues [24] harnessed flower-shaped graphene (FG) synthesized via transformer-coupled plasma-enhanced chemical vapor deposition as a carrier for crafting composite photocatalysts. ZnS particles were grown on the surface of FG through a hydrothermal method. The research findings highlight the ability of FG's flower-like structure to facilitate light absorption. Comparative to pristine ZnS photocatalysts, the FG-ZnS nanocomposite material demonstrates enhanced photocatalytic hydrogen production activity.Baniagaet al. [25] utilized latex from the rubber tree as a raw material to synthesize greenly, yielding ZnS nanoparticles with an average diameter of 80 nm. Experimental analysis suggests that these ZnS nanoparticles may exhibit correlated degradation efficiency towards organic dyes such as methylene blue. The optimal conditions for photocatalytic degradation of methylene blue and other organic dyes were found to be dependent on pH and temperature.

Ye and his research team [26] employed a straightforward chemical precipitation method to synthesize cubic-phase ZnS nanoparticles. Photocatalytic experiments revealed that pure ZnS nanoparticles exhibited significantly higher photocatalytic activity for the degradation of MO and MR dyes compared to the degradation of MB. Moreover, ZnS nanoparticles generated XO dyes, which efficiently degraded ZnO nanoparticles. The possible photocatalytic mechanisms for degrading various dyes in the presence of ZnS nanoparticles were analyzed based on electrochemical measurements and photocatalytic experiments.

3.3**Applications in Biomedicine**

Zinc sulfide (ZnS) nanoparticles find versatile utility in the realm of biomedicine, serving as bioimaging agents, drug delivery vehicles, and molecular probes. Moreover, ZnS nanoparticles are under investigation for therapeutic applications, including cancer treatment.

Cowcles and colleagues [27] reported an innovative approach using ZnS nanoparticles as fluorescent signal transducers in lieu of traditional methods for immunoassays of Escherichia coli O157:H7 in tap water samples. The fluorescence signal is generated by the binding of zinc ions released from the nanoparticle labels with the zinc ion-sensitive fluorescence indicator Fluozin-3. In this assay, ZnS nanoparticles with a diameter of approximately 50 nm were synthesized, bioconjugated, and employed for the detection of E. coli O157:H7.

Wang and his team [28] employed a hydrothermal synthesis method to create CdTeSe/ZnS core-shell quantum dots with near-infrared output and exceptional photothermal properties. Utilizing a blue laser as the irradiation source, quantum dot (QD) fluorescence imaging allows precise calibration of treatment areas. Under the influence of photothermal and photodynamic effects induced by the quantum dots, apoptosis was induced in Huh7 liver cancer cells.

3.4Frictional Applications

Zinc sulfide (ZnS) nanoparticles exhibit exceptional anti-wear and friction-reducing properties when employed as lubricant additives. To ensure stable dispersion in base lubricants, ZnS is typically surface-modified before integration.

Kumara and colleagues [8] reported the use of 12-alkylthiol-modified oil-suspended and optically transparent ZnS nanoparticles (NPs) with a nominal diameter of 4 nm as anti-wear additives in nonpolar base oils. ZnS NPs form a transparent and long-term stable suspension in PAO4 lubricating oil. At concentrations of 0.5 wt% or 1.0 wt% in PAO4 oil, ZnS NPs demonstrate excellent friction and wear protection properties. The wear reduction achieved by the synthesized ZnS NPs is substantial, amounting to a remarkable 98% decrease compared to pure PAO4 base oil.

Ugur and collaborators[29] investigated the frictional performance of 1-octanethiol-terminated ZnS nanoparticles (OT-ZnS) as lubricant additives.

Experimental results reveal that the addition of OT-ZnS NPs in a 10W base oil increases its viscosity and reduces the contact angle (CA) value. The inclusion of OT-ZnS significantly enhances the anti-wear properties of the base oil, particularly under higher pressures.

4.**Conclusion and Outlook**

With the advancement of technology, future research on the preparation and application of ZnS nanomaterials should focus on the following aspects:

(1) The nanostructure, morphology, and size of ZnS have a significant impact on its physicochemical properties, and different application fields have distinct demands for the performance of ZnS nanomaterials. Future research will continue to seek improved methods for precise control over the size, shape, and structure of ZnS nanoparticles to meet specific application requirements. Researchers will strive to develop more environmentally friendly preparation methods, reducing waste and the emission of hazardous substances, in support of sustainable development goals.

(2) Doping of ZnS nanomaterials can alter their crystal structure, reduce the bandgap, and enhance the electrical, optical, and photocatalytic properties of ZnS. Therefore, in addition to the existing ZnS doping approaches, further investigation into the influence of additional element doping on the material's performance is warranted to realize the multifunctionality of ZnS nanomaterials. Furthermore, self-assembly techniques hold promise for organizing ZnS nanoparticles into ordered structures and photonic crystals.

(3) With the continuous development of nanotechnology, ZnS nanomaterials have demonstrated significant potential in emerging fields such as biomedicine, food science, agriculture, and more. Targeted and in-depth research should be conducted to explore the application of ZnS nanoparticles in areas like wearable electronic devices, environmental remediation, and novel display technologies. Continuous exploration of the immense potential of ZnS nanomaterials will drive ongoing innovation.

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