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OPTICAL CHARACTERIZATION OF ZnS NANOPARTICLES PREPARED BY THE SILAR METHOD USING POLYMER-DERIVED BIOCHAR ADDITIVES

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Zinc sulfide (ZnS) is a wide band gap II-VI semiconductor with significant potential for optoelectronic and ultraviolet (UV) sensing applications. In this study, ZnS nanoparticles were synthesized via the Successive Ionic Layer Adsorption and Reaction (SILAR) method using a polymer-derived biochar additive obtained from agricultural waste. The environmentally friendly synthesis route enables controlled nucleation and growth of ZnS nanoparticles through repeated SILAR cycles. Optical properties were investigated by UV-Vis spectroscopy in the wavelength range of 200-900 nm. The absorption spectra reveal strong absorption in the UV region and high transparency in the visible range, indicating the formation of nanoscale ZnS. The optical band gap was estimated from the absorption edge in the UV-Vis spectra, was found to be in the range of 3.7-3.9 eV, which is larger than that of bulk ZnS due to quantum confinement effects. The results demonstrate that biochar plays a key role in improving particle homogeneity and optical performance. The synthesized ZnS nanoparticles show strong potential for application in UV photodetectors, optoelectronic devices and sustainable functional coatings.

Keywords: ZnS nanoparticles, SILAR method, biochar, polymer-derived additives, UV-Vis spectroscopy, wide band gap semiconductors.

INTRODUCTION

Wide band gap semiconductor nanomaterials have attracted extensive research interest over the last two decades due to their size-dependent optical and electronic properties [1]. Among II-VI semiconductors, zinc sulfide (ZnS) is one of the most intensively studied materials because of its direct band gap (~3.6 eV), low toxicity, chemical stability and high refractive index [2,3]. These characteristics, photocatalysis, ultraviolet photodetectors, sensors and light-emitting devices [3,6]. In addition to its intrinsic optoelectronic properties, ZnS exhibits polymorphism in cubic (zinc blende) and hexagonal (wurtzite) crystal structures, both of which influence its band structure and optical transitions [13]. The ability to tailor crystal phase, defect density and surface states at the nanoscale further expands its applicability in advanced photonic and energy-related systems. Recent studies have emphasized that surface engineering and interface modification play decisive roles in determining carrier dynamics, recombination rates and light-matter interaction efficiency in ZnS-based nanostructures [7].

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Recent studies over the past decade have increasingly emphasized the importance of interface engineering and surface-functionalized growth in tailoring the optical performance of ZnS nanostructures. Although the SILAR technique has been widely employed for the controlled fabrication of II-VI semiconductor thin films and nanoparticles, most investigations have primarily focused on dopant incorporation or surfactant-assisted stabilization [4,5,15]. The influence of bio-derived carbonaceous matrices on nucleation kinetics and band structure modulation remains comparatively underexplored. In particular, polymer-derived biochar has not been systematically evaluated as a multifunctional growth-directing additive for ZnS nanoparticle synthesis. Therefore, integrating sustainable carbon materials into low-temperature deposition strategies represents a significant research gap that the present study aims to address. These effects strongly depend on synthesis conditions, particle size, morphology and surface chemistry, which collectively determine the electronic band structure and defect density of ZnS nanostructures. Therefore, controlled and reproducible synthesis strategies are essential for tailoring ZnS nanoparticle properties. Precise control over nucleation kinetics and growth mechanisms is particularly critical for achieving uniform particle size distribution and minimizing structural defects. Variations in precursor concentration, reaction time, pH and temperature directly affect particle morphology and consequently optical absorption behavior. Furthermore, surface passivation strategies are frequently employed to suppress non-radiative recombination centers, thereby enhancing optical efficiency and stability.

Numerous synthesis techniques have been reported for ZnS nanomaterials, including sol-gel processing, chemical precipitation, hydrothermal and solvothermal routes, microwave-assisted synthesis and successive ionic layer adsorption and reaction (SILAR). Among these, the SILAR method offers distinct advantages such as simplicity, low cost, room-temperature processing and precise control over material growth through repeated adsorption-reaction cycles. The layer-by-layer growth mechanism inherent to the SILAR technique enables fine tuning of film thickness and nanoparticle loading by simply adjusting the number of deposition cycles. This method also facilitates heterogeneous nucleation on functionalized substrates, making it highly suitable for composite and hybrid nanostructure fabrication. Compared to high-temperature hydrothermal routes, SILAR provides improved energy efficiency and compatibility with environmentally benign processing conditions.

In parallel with advances in nanomaterial synthesis, there is growing emphasis on green chemistry and sustainable material processing. Biochar, a carbon-rich material obtained from agricultural waste, has emerged as a promising polymer-derived additive for nanoparticle synthesis. Its porous structure, high surface area and abundance of functional groups make it an effective stabilizing and structure-directing agent. Moreover, the use of biochar contributes to waste valorization and reduces environmental impact. The incorporation of biochar into semiconductor synthesis introduces a multifunctional carbonaceous matrix capable of modulating charge transfer processes and enhancing structural stability. Owing to its tunable porosity and surface chemistry, biochar can act simultaneously as a nucleation template, dispersing agent and electron mediator. Such synergistic effects are particularly attractive for developing sustainable nanocomposites with improved optical and electronic performance.

In this context, the present study aims to develop an environmentally sustainable strategy for synthesizing ZnS nanoparticles via the SILAR technique in the presence of polymer-derived biochar additives. Particular emphasis is placed on understanding the influence of the biochar matrix on nucleation behavior, particle distribution and optical band gap modification. By systematically analyzing UV-Vis absorption characteristics and evaluating quantum confinement effects, this work seeks to establish a clear structure-property relationship. The findings are expected to contribute to the advancement of green nanotechnology approaches for high-performance optoelectronic and ultraviolet-responsive materials.

EXPERIMENTAL

Zinc chloride ($ZnCl_2$, analytical grade) and sodium sulfide nonahydrate ($Na_2S{\cdot}9H_2O$, analytical grade) were used as zinc and sulfur precursors, respectively. Deionized water was employed for all solution preparations. All experimental procedures were carried out under ambient laboratory (≈25°C, atmospheric pressure). To ensure experimental reliability, precursor solutions were freshly prepared prior to each synthesis cycle. Biochar was obtained from agricultural waste and used as a polymer-derived additive further chemical modification.

Biochar was produced via controlled pyrolysis of agricultural waste under limited oxygen conditions. The selected pyrolysis temperature range was chosen to maximize carbon yield while preserving surface functional groups responsible for metal ion coordination. The obtained material was stored in airtight containers to prevent moisture adsorption prior to use. The resulting carbonaceous material was finely ground to obtain a uniform powder and subsequently dispersed in deionized water under continuous stirring to form a stable suspension. The porous structure and surface functional groups of biochar formation.

ZnS nanoparticles were synthesized using the successive ionic layer adsorption and reaction (SILAR)method [10]. The deposition process was carried out on thoroughly cleaned glass substrates using two successive SILAR cycles under ambient conditions. Each immersion step was optimized to allow sufficient ion adsorption without promoting homogeneous precipitation in the bulk solution. The sequential adsorption-reaction mechanism enables surface-confined ZnS formation directly on the biochar matrix. In a typical procedure, a fixed amount of biochar (5 g) was dispersed in deionized water under constant stirring to ensure homogeneous suspension. Aqueous solutions of $ZnCl_2$ (0.1 M, 200 ml) and $Na_2S{\cdot}9H_2O$ (0.1 M, 55 ml) were introduced sequentially into the biochar suspension. The precursor concentration was selected to balance nucleation density and particle growth rate, thereby preventing excessive aggregation. Maintaining moderate ionic strength is essential for obtaining nanoscale crystallites with controlled optical characteristics.

Each SILAR cycle consisted of the adsorption of Zn^{2+} ions onto the biochar surface, followed by their reaction with sulfide ions to form ZnS nanoparticles. The number of deposition cycles was used as the primary growth parameter to regulate nanoparticle loading and optical density. After each adsorption-reaction step, the material was rinsed with deionized water to remove excess and weakly bound ions. The process was repeated for multiple SILAR cycles to control nanoparticle deposition and distribution on the biochar matrix.

After completion of the synthesis, the resulting ZnS/biochar composite was collected, thoroughly washed with deionized water and dried at room temperature. The optical properties of the synthesized ZnS nanoparticles were investigated using UV-Vis absorption spectroscopy. Measurements were performed over a wavelength range of 200-900 nm to evaluate the absorption behavior in the ultraviolet and visible regions [9,19]. The optical band gap was evaluated based on the absorption edge analysis of the recorded UV-Vis spectra.

The growth mechanism of ZnS nanoparticles in the presence of biochar can be interpreted within a heterogeneous nucleation framework. The oxygen-containing functional groups on the biochar surface facilitate electrostatic interaction with Zn^{2+} ions during the adsorption step, forming localized ion-rich regions. Upon exposure to sulfide ions, these sites act as confined nucleation centers, promoting surface-bound ZnS formation rather than bulk precipitation. This mechanism effectively suppresses uncontrolled aggregation and enhances particle dispersion. As a result, the layer-by-layer SILAR process combined with the porous carbon matrix enables improved regulation of crystallite size and optical uniformity.

RESULTS AND DISCUSSION

During the SILAR synthesis process, the formation of a dark-colored precipitate was observed after several cycles, indicating successful ZnS nanoparticle formation (Figure 1).

The photographic image of the precipitate confirms effective nucleation and growth of ZnS in the presence of biochar.

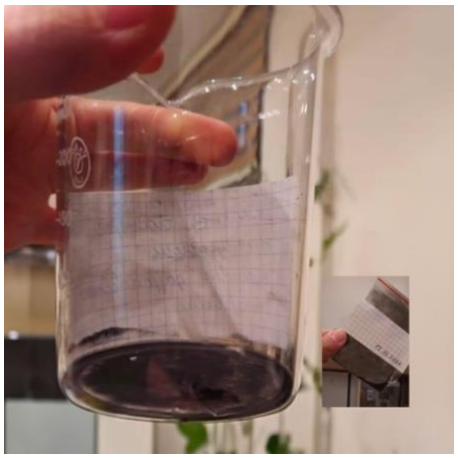

Figure 1. Photograph of the dark-colored ZnS nanoparticle precipitate formed during the SILAR synthesis process in the presence of biochar.

The biochar matrix provides numerous active sites for ion adsorption, leading to uniform particle distribution and reduced agglomeration. The UV-Vis absorption spectrum of the synthesized ZnS nanoparticles exhibits a pronounced absorption band in the ultraviolet region.

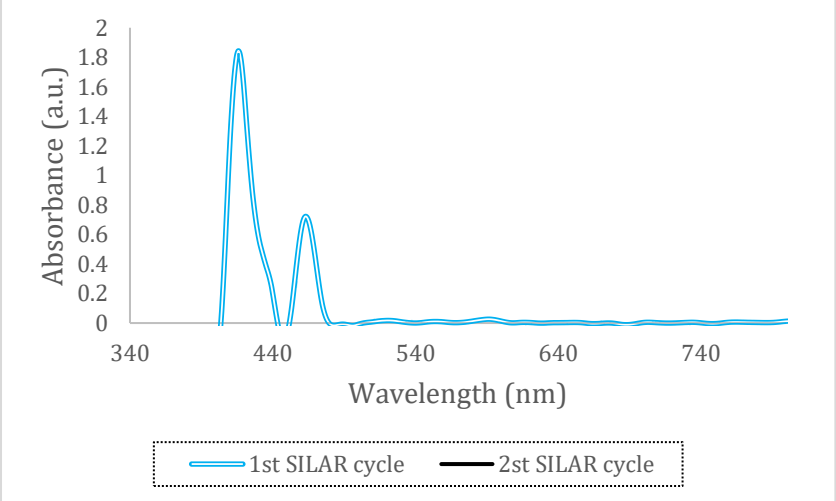

Figure 2. UV-Vis absorption spectra of ZnS nanoparticles synthesized by the SILAR method in the presence of biochar after the 1st and 2nd SILAR cycles.

A sharp decrease in absorption intensity is observed above ~400 nm [2,3]. This behavior is characteristic if wide band gap semiconductor materials and confirms the nanoscale nature of the synthesized ZnS.

The high transparency observed in the visible region is particularly important for optoelectronic and window-layer applications. The sharp absorption edge suggests good crystallinity and relatively narrow particle size distribution.

The calculated band gap values lie in the range of 3.7-3.9 eV, which is higher than that of bulk ZnS [9,19]. The observed band gap widening compared to bulk ZnS (~3.6 eV) suggests pronounced quantum confinement effects due to reduced crystallite dimensions. The incorporation of polymer-derived biochar regulates nucleation kinetics and suppresses excessive particle growth, leading to improved optical homogeneity and reduced defect-related trap states. These features are particularly beneficial for ultraviolet-responsive optoelectronic applications. The observed band gap widening compared to bulk ZnS (~3.6 eV) can be attributed to pronounced quantum confinement effects associated with reduced

crystallite dimensions. Similar band gap shifts have been reported for chemically synthesized ZnS nanoparticles prepared under low-temperature conditions [10,14]. However, the relatively higher band gap values obtained in this study suggest a narrower particle size distribution and improved structural homogeneity. The presence of biochar likely contributes to this effect by providing spatial confinement and minimizing defect-induced mid-gap states. Furthermore, the sharp absorption edge indicates reduced structural disorder, which is critical for high-performance ultraviolet-responsive devices. Similar trends have been widely reported for ZnS and other II-VI semiconductor nanoparticles synthesized via low-temperature chemical routes [16].

Biochar plays a crucial role in controlling both the growth mechanism and optical properties of ZnS nanoparticles. The functional groups on the biochar surface enhance interactions with Zn^{2+} and S^{2-} ions, promoting uniform nucleation [11,12,18]. In addition, the porous carbon matrix acts as a physical barrier against excessive particle aggregation, resulting in improved optical uniformity and stability.

The combination of sustainable biochar additives and the SILAR technique provides an effective strategy for green synthesis of functional semiconductor nanomaterials.

The strong ultraviolet absorption, wide band gap and high visible transparency of the synthesized ZnS nanoparticles make them promising candidates for ultraviolet photodetectors, optoelectronic devices, UV-blocking coatings and sensor technologies. The environmentally friendly synthesis approach further enhances their suitability for large-scale and sustainable applications.

CONCLUSION

ZnS nanoparticles were successfully synthesized using the SILAR method with polymer-derived biochar additives. UV-Vis spectroscopic analysis confirmed strong UV absorption and high transparency in the visible region. The estimated optical band gap of 3.7-3.9 eV indicates pronounced quantum confinement effects. Biochar was shown to play a key role in improving nanoparticle homogeneity and optical performance. From a broader perspective, the integration of polymer-derived biochar with the SILAR technique demonstrates a scalable and environmentally responsible route for advanced semiconductor fabrication. The synergistic interaction between the carbonaceous matrix and ZnS nanoparticles enables enhanced optical tuning while maintaining structural stability. Future work may focus on correlating biochar concebtration with electronic transport behavior, photoluminescence characteristics and device-level performance. Such investigations would further validate the applicability of this sustainable synthesis strategy in next-generation optoelectronic and ultraviolet detection systems. The results demonstrate that this green synthesis route is a promising approach for producing high-quality ZnS nanoparticles for advanced optoelectronic applications.

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