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A Review Article: Progress in Nanostructures Based on Zinc Sulfide as Photocatalysts for Wastewater Treatment and Antimicrobial Effectiveness

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Abstract:

The incessant growth of the world's population has resulted in a persistent escalation of environmental pollution, which poses a significant threat to human health. Various industries, such as textiles, leather, pharmaceuticals, and plastics, discharge harmful, non-biodegradable, and persistent organic pollutants, including dyes, pharmaceuticals, and pesticides, into water bodies. Consequently, the purification of industrial wastewater using environmentally friendly technologies has become a crucial focus for global research. Photocatalytic technology, a pioneering approach rooted in AOP (Advanced Oxidation Processes), emerges as a sustainable solution to address the escalating environmental challenges. In the field of photocatalysis, the photocatalyst is a crucial component, typically composed of a semiconductor material with high solar light absorption capacity and conductivity for photogenerated charge carriers. Zinc sulfide (ZnS), an n-type semiconductor with diverse morphologies and band gap energies (Eg = 3.2–3.71 eV), has been identified as a particularly promising photocatalyst for the removal of organic pollutants from wastewater, especially under (UV, Vis) and sunlight irradiation during wastewater treatment. This review comprehensively examines the impact of various synthesis parameters, such as the type and concentration of precursors, dosages of capping agents, reaction time and temperature, metal doping, ZnS concentration in heterostructures, etc., and properties, including particle size, morphology, band gap energy, and surface properties, on the photocatalytic efficacy of ZnS-based photocatalysts in degrading diverse organic pollutants. Zinc sulfide (ZnS) nanoparticles were systematically evaluated for their antimicrobial properties against four pathogenic strains. The discussion is structured to offer a comprehensive understanding of the intricate interplay between synthesis conditions and resulting properties, with the aim of advancing the optimization of ZnS-based photocatalysts for effective wastewater treatment applications.

Keywords: ZnS nanostructures; organic pollutants; wastewater treatment; antimicrobial activity.

مقالة مراجعة: التقدم المحرز في الهياكل النانوية المعتمدة على كبريتيد الزنك كمحفزات ضوئية لمعالجة مياه الصرف الصحي والفعالية المضادة للميكروبات

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مستخلص:

أدى النمو السكاني المستمر في العالم إلى تصاعد مستمر في التلوث البيئي مما يشكل خطرا كبيرا على صحة الإنسان. تقوم الصناعات المختلفة مثل المنسوجات والجلود والأدوية والبلاستيك بإطلاق الملوثات العضوية الضارة وغير القابلة للتحلل والملوثات العضوية الثابتة بما في ذلك الأصباغ والأدوية والمبيدات الحشرية إلى المسطحات المائية. ونتيجة لذلك، أصبحت تنقية مياه الصرف الصناعي باستخدام تقنيات صديقة للبيئة محورًا حاسمًا للأبحاث العالمية. تظهر تقنية التحفيز الضوئي، وهي نهج رائد متجذر في AOP (عمليات الأكسدة المتقدمة) كحل مستدام لمواجهة التحديات البيئية المتصاعدة. في مجال التحفيز الضوئي، يعد المحفز الضوئي مكونًا حاسمًا ويتكون عادةً من مادة شبه موصلة ذات قدرة عالية على امتصاص الضوء الشمسي وموصلية لحاملات الشحن المولدة ضوئيًا. تم تحديد كبريتيد الزنك (ZnS)، وهو أشباه الموصلات من النوع n مع أشكال متنوعة وطاقات فجوة النطاق (على سبيل المثال = 3.2–3.71 فولت)، باعتباره محفزًا ضوئيًا واعدًا بشكل خاص لإزالة الملوثات العضوية من مياه الصرف الصحي، خاصة تحت (الأشعة فوق البنفسجية، والضوء المرئي) وتشعيع أشعة الشمس أثناء معالجة مياه الصرف الصحي. تبحث هذه المراجعة بشكل شامل تأثير معلمات التوليف المختلفة مثل نوع وتركيز السلائف، وجرعات عوامل السد، ووقت التفاعل ودرجة الحرارة، ومنشطات المعادن، وتركيز ZnS في الهياكل المتغايرة، وما إلى ذلك، والخصائص، بما في ذلك حجم الجسيمات، والتشكل، طاقة فجوة النطاق، وخصائص السطح، على فعالية التحفيز الضوئي للمحفزات الضوئية المعتمدة على ZnS في تحلل الملوثات العضوية المتنوعة. تم تقييم الجسيمات النانوية من كبريتيد الزنك (ZnS) بشكل منهجي لخصائصها المضادة للميكروبات ضد أربع سلالات مسببة للأمراض. تم تنظيم المناقشة لتقديم فهم شامل للتفاعل المعقد بين ظروف التوليف والخصائص الناتجة بهدف تعزيز تحسين المحفزات الضوئية المستندة إلى ZnS لتطبيقات معالجة مياه الصرف الصحي الفعالة.

الكلمات المفتاحية: الهياكل النانوية ZnS؛ الملوثات العضوية؛ معالجة مياه الصرف الصحي؛ النشاط المضاد للميكروبات.

1. Introduction

Nanoscience is a specialized field in science that focuses on thoroughly studying the properties of materials at the nanoscale. The main emphasis is on carefully examining the unique characteristics and size-dependent properties found in solid-state materials [1-3].

Various methodologies exist for the preparation of nanomaterials, encompassing conventional chemical approaches as well as environmentally sustainable green methods employing extracts derived from plant sources [4]. The synthesis of nanomaterials involves the manipulation of materials at the nanoscale, and the choice of method holds significant implications for both the efficiency of the process and its ecological impact [5]. Traditional chemical methods, rooted in well-established principles of chemistry, are juxtaposed with emerging green approaches that leverage the inherent properties of plant extracts to foster the synthesis of nanomaterials in an eco-friendly manner. This duality in methodologies underscores the dynamic landscape of nanomaterial preparation, where the pursuit of technological advancement converges with the imperative to mitigate environmental impact [6,7].

Contamination of wastewater with non-biodegradable toxic and organic pollutants poses a significant challenge for both the environment and public health, particularly in the context of industrial activities such as textiles, plastics, paper, food, and cosmetics [8-19].

Approximately 20% of total industrial polluted water is attributed to the discharge of industrial wastewater, primarily from the textile sector [20].

The presence of even minute concentrations of organic dyes in water can have adverse effects on the environment and human health, including skin irritations, respiratory issues, and, in severe cases, serious illnesses such as cancer [21,22].

A considerable portion of industrial dyes, particularly azo dyes with aromatic structures, exhibits poor degradability under natural conditions, necessitating effective wastewater treatment before discharge [23,24].

Nanoparticles are employed to enhance the intrinsic characteristics of specific materials intended for medical applications, notably in the realms of anti-cancer and dental materials. This utilization involves leveraging the unique properties and dimensions of nanoparticles to augment the performance and efficacy of said materials, thereby contributing to advancements in medical science and therapeutic modalities [25,26].

Nanomaterials possess many optical, electrical, and magnetic properties that distinguish them from other materials due to the large surface area that these materials possess [27-30].

The escalating consumption of pharmaceuticals, particularly antibiotics, has led to the detection of a significant residue in surface water, soil, sewage, and wastewater from pharmaceutical industries. The prolonged presence of pharmaceutical contaminants in water systems contributes to the development of antibiotic resistance in pathogens and various microorganisms, necessitating the removal of pharmaceutical products and other organic pollutants from wastewater to mitigate environmental and public health risks [31,32].

To address the aforementioned concerns, advanced oxidation processes (AOPs) have emerged as a promising approach, utilizing highly reactive oxidant species such as hydroxyl and superoxide ion free radicals to decompose organic pollutants into harmless by-products such as water and carbon dioxide [33].

Photocatalysis, a specific AOP utilizing semiconductor materials as catalysts [34], has gained attention as a sustainable and efficient technology for environmental remediation. Semiconductor-based photocatalysis, particularly employing metal sulfides nanostructures, stands out as a viable method due to its simplicity, ecological friendliness, low cost, and high efficiency [35,36].

Among the class of transition metal semiconductors, zinc sulfide (ZnS) has gained prominence as a photocatalyst, possessing attributes such as a wide band gap, thermal stability, high electronic mobility, water insolubility, non-toxicity, and cost-effectiveness [37-39].

Despite its effectiveness under UV light irradiation, ZnS nanostructures face limitations in visible and sunlight due to intrinsic defects and wide band gap energies, resulting in suboptimal photocatalytic performance [40-43].

Various strategies, including morphology engineering [44,45] doping [46,47] defect engineering [48-50], dye sensitization [51], and heterostructures construction [52], have been employed to enhance ZnS photocatalytic efficiency.

This review aims to consolidate and update information from the past five years on ZnS-based photocatalysts, specifically focusing on their application in degrading diverse organic pollutants under sunlight irradiation and (UV, Vis). The objective is to assess the photocatalytic efficacy of ZnS-based materials in treating of organic pollutants, with implications for potential enhancements in wastewater treatment efficiency.

2. ZnS Nanostructures Photocatalysts for Organic Pollutants Degradation

Zinc sulfide (ZnS) is recognized as a semiconductor with wide band gap, with a band gap energy spanning from 3.25 to 3.74 eV [53], for the cubic structure and 3.52 to 3.64 eV [54], for the hexagonal structure. In the hexagonal structure, there is a significant exciton binding energy of (40 meV) [55]. The reported band gap energy (Eg) for ZnS varies from 2.5 eV [56] to 4.64 eV [57], but the majority of values tend to cluster around Eg = 3.21–3.71 eV, as depicted in Figure 1. Noteworthy is ZnS's heightened sensitivity to UV light absorption ($\lambda < 340$ nm), accounting for about 4% of total sunlight.

To expand the applicability of ZnS photocatalysts into the visible light range ($\lambda \geq 420$ nm) within the solar spectrum, efforts have focused on reducing the band gap energy and adjusting the positions of the conduction band (CB) and valence band (VB) edges. Various strategies have been explored, including altering morphology [56]. doping with metal/nonmetal ions [57,58], creating semiconductor nanocomposites [59]., and controlling surface defects [60].

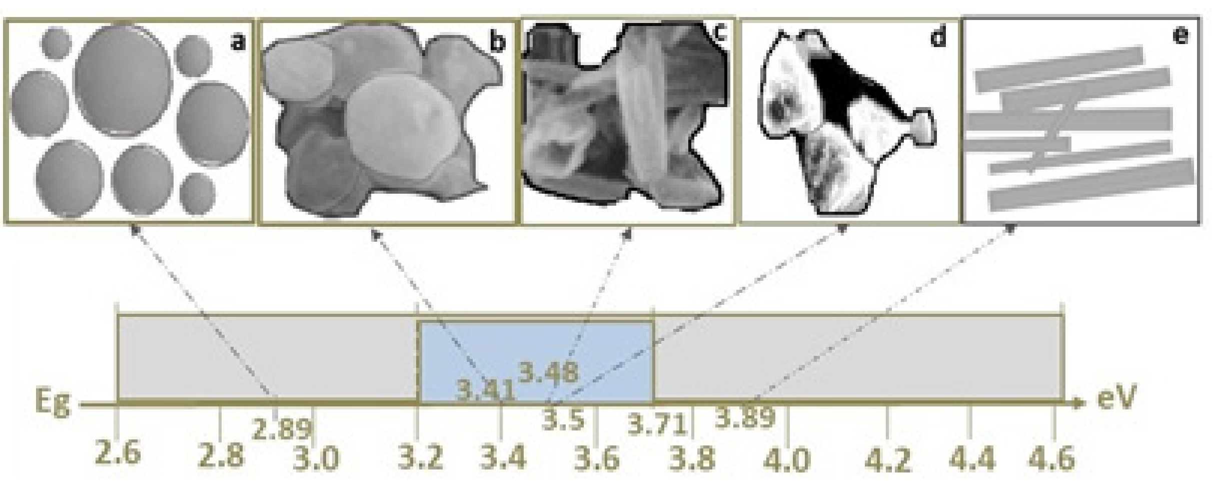


Figure 1. Band gap energy values and the variation with ZnS NPs' morphologies: spheres (**a**), nanosheets (**b**), nanotubes (**c**), random (**d**), and rod-shape (**e**).

Achieving modulation of ZnS photocatalyst characteristics requires a thoughtful selection of a straightforward, efficient, environmentally friendly, and economically feasible synthesis method, coupled with easy adjustments to operational parameters. Additionally, during the photodegradation process, it is crucial to consider several key factors. These factors encompass the amount of photocatalyst used, the type and concentration of the specific pollutant targeted, and the attributes of the irradiation source, including both its type and intensity using hydrothermal and refluxing methods for (Methylene Blue, MB and Tropaeolin O, TO) [21,61] as presented in Table 1.

Table 1. Organic pollutants degradation in wastewater treatment of ZnS-based photocatalysts

Photocatalyst	Structure	Synthesis Method	Pollutant Conc. (mg/L)	Catalyst Dosage (g/L)	Light Source	η* (%)	t (min)
ZnS Au-ZnS Ag-ZnS	0D NsS QDs	HT	MB (30)	0.05	UV (6 W lamp)	72.5 96.7 92.6	180
ZnS Mn-ZnS	0D NsS QDs	Refluxing	TO (12.65)	0.5 g	UV (8 W lamp)	92.6 94	30 90

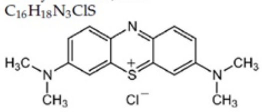
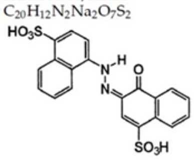
2.1. Zero Dimensional ZnS-Based Nanostructures

(0D) nanostructures, encompassing entities like nanodots, quantum dots, polymer dots, magnetic nanoparticles and fullerene exhibit nanoscale dimensions in all three directions, primarily manifesting as spherical or quasi-spherical particles with a diameter below 100 nm. These materials possess structural characteristics, including high specific surface areas and ultra-small dimensions, resulting in a greater number of active sites per mass unit and quantum confinement effects within specific dimensions [62].

Given their outstanding optical and electronic properties, along with attributes such as non-toxicity, physicochemical stability, and cost-effective synthesis procedures, ZnS quantum dots (QDs) have garnered increasing attention as promising photocatalysts for removing organic pollutants from wastewater.

To address the challenge posed by the wide band gap energy of ZnS QDs, researchers frequently employ a strategy involving the doping of ZnS QDs with suitable elements, such as metal atoms or ions. This approach aims to facilitate electronic transitions at energies corresponding to visible light wavelengths [58] as presented in Table 2. The dopants not only serve as centers for visible light absorption but also function as trapping sites for charge carriers (electrons or holes). This dual role helps prevent recombination and promotes the necessary charge separation crucial for efficient photocatalytic reactions [21,51].

Table 2. The photocatalytic, structural and optical properties of undoped and metal doped ZnS QDS' photocatalysts.

Photocatalyst	Eg (eV)	Particle Size (nm)	Photodegradation			
			Dye			
			Chemical Formula and Structure	λ_{max} (nm)	η* (%)	Time (min)
ZnS QDs	4	4.2	Methylene Blue, MB $C_{16}H_{18}N_3ClS$ 	665	61 (Vis)	180
ZnS QDs	4.64	4.3			72.5	180
Ag-ZnS QDs	3.06	4.7			92.6	
Au-ZnS QDs	2.4	5.6			96.7	
ZnS QDs	3.7	21–44	Acid red 14, AR14 $C_{20}H_{12}N_2Na_2O_7S_2$ 	515	85.4	180
Gd-ZnS QDs	3.45	20–34			91.1	

η* is pollutant degradation efficiency after t min of irradiation.

2.2. One Dimensional ZnS-Based Nanostructures

In recent years, there has been a surge in scientific interest surrounding one-dimensional nanostructures (1D NSs), which include nanospheres, nanorods, nanotubes, and nanowires. These structures possess one dimension exceeding the nano-scale range (1–100 nm), while the other two dimensions remain within the nanoscale, leading to distinctive characteristics. The growing fascination with 1D NSs can be attributed to their diverse morphologies, chemical compositions, and structural variations. Considerable efforts have been dedicated to synthesizing nanostructured ZnS photocatalysts, with a specific emphasis on achieving controlled morphologies. These morphologies encompass nanospheres [56] nanotubes, nanosheets [63] and nanorods [56]. Among the noteworthy 1D ZnS NSs, nanotubes stand out due to their hollow mesoporous structure, providing a significant specific surface area. This feature contributes to enhancing their optoelectronic properties, including band gap energy (Eg) and electron conductivity. In contrast, nanorods exhibit solid structures with lengths typically ranging between (10) and (20) nm, often featuring hexagonal cross-sections. The investigation of core-shell nanorod structures has been extensive [64].

Figure 1 illustrates a variety of ZnS NS morphologies along with the corresponding values of band gap energy.

The schematic representation of the photodegradation mechanism for Methylene Blue (MB) dye utilizing one-dimensional (1D) ZnS nanosheet (NS) catalysts is delineated in Figure 2.

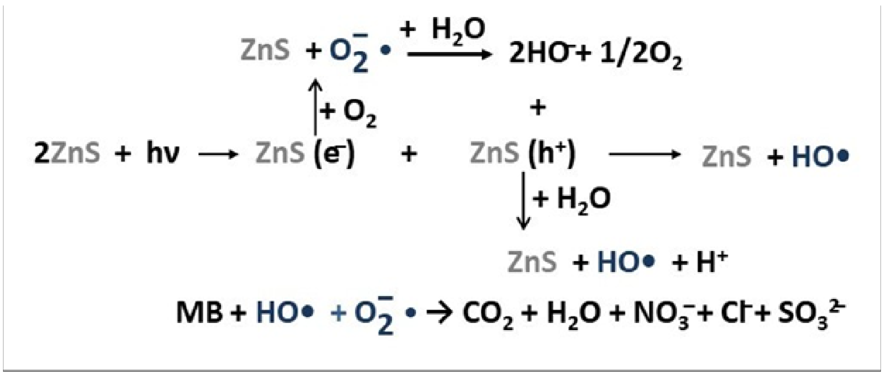


Figure 2. The mechanism of the reaction proposed for MB dye degradation under UV irradiation, in presence of one Dimensional ZnS photocatalyst.

Upon exposure to UV radiation, photo-induced electron-hole pairs are engendered on the valence band (VB) and conduction band (CB) of the ZnS photocatalyst, and these pairs are subsequently conveyed to the surface of the ZnS nanoparticles (NPs). The ensuing interaction of photogenerated electrons (e-) and holes (h+) with adsorbed water and oxygen molecules on the ZnS NPs' surface results in the production of superoxide anion radicals ($O_2^{-\bullet}$) and hydroxyl radicals ($HO^{\bullet}$). These highly reactive species function as oxidizing agents, leading to the decomposition of MB dye molecules into carbon dioxide (CO_2), water (H_2O), and another salt ions [65].

The influence of capping agents and silver (Ag) doping on the morphology, photocatalytic and optoelectronic characteristics of ZnS NS photocatalysts has been extensively investigated in various studies. Notably, recent works [57]. have explored the comparative photocatalytic activities of ZnS and Ag-ZnS catalysts in the degradation of different dyes. These investigations were conducted under UV and irradiation of sunlight conditions, providing insights into the nuanced impact of Ag-doping and capping agents on the catalytic performance of ZnS NS photocatalysts.

3. ZnS Nanostructures as antibacterial agents

Antibacterial compounds are distinguished by their ability to eliminate bacteria in a specific area or hinder their growth, all while demonstrating minimal toxicity to surrounding healthy tissues. Many antibacterial agents originate from entirely natural sources are created through chemical alterations of natural compounds, including β-lactams [66-69]. Furthermore, entirely synthetic antibiotics, such as sulfonamides, have been formulated for their antibacterial efficacy [70].

The sensitivity of bacteria to nanoparticles (NPs) extends beyond the structural features of the cell wall in both gram-positive and gram-negative bacteria [71]. Instead, bacterial susceptibility or resistance to NPs is intricately connected to the characteristics and composition of the nanoparticles themselves. For instance, the response to copper oxide nanoparticles (CuO NPs) varies among different bacterial strains. Specifically, Escherichia coli (gram-negative) demonstrates high susceptibility, whereas Staphylococcus aureus (gram-positive) and Bacillus subtilis (gram-positive) exhibit comparatively lower susceptibility to CuO NPs [64].

The contemporary surge in worldwide attention towards the antibacterial attributes of zinc compound nanoparticles, particularly those composed of zinc sulfide (ZnS-NPs), has attracted substantial interest [72]. Zinc, an essential trace element, assumes an indispensable role in nearly all biological processes, although bacteria necessitate trace quantities of zinc for essential functions, an abundance of this metal can induce deleterious effects on them [73].

4. Conclusions

In recent decades, a variety of ZnS and ZnS-based photocatalysts have emerged, designed for a range of applications such as wastewater and air treatment, CO2 reduction, and hydrogen (H_2) production through photoelectrolytic water splitting. This review specifically concentrates on the latest developments in ZnS-based photocatalysts customized for wastewater treatment. It highlights a significant increase in scholarly efforts within a relatively short span of five years. The accumulated research represents a valuable source of knowledge for the wider academic community involved in this specific field.

Extensive research has been dedicated to enhancing the photocatalytic activity of ZnS within the visible light range. Various approaches, including metal doping, morphology engineering and heterojunction construction, have been explored. A significant focus lies on the crucial task of designing stable ZnS-based heterostructures. This is vital not only for boosting the photocatalytic effectiveness of individual ZnS photocatalysts, which are inherently prone to photo-corrosion, but also for extending the photocatalytic response into the visible region of the electromagnetic spectrum.

The distinct morphologies exhibited by ZnS-based photocatalysts, manipulated through variations in synthesis parameters, profoundly impact their photocatalytic performance. This impact is evident in the distribution of the photogenerated electron-hole pairs and the adsorption capacity for reactant molecules. Therefore, the preparation methods for ZnS-based photocatalysts need to be simple, cost-effective, and energy-efficient, with feasibility for the application in industrial-scale. Preferably, environmentally benign techniques are favored for their ease and economic viability in addressing both the removal of organic pollutants and the utilization of plant wastes from wastewater.

Crucially, thorough investigations into the reusability and photostability of ZnS-based photocatalysts are imperative. These studies aim to assess the catalysts' ability to undergo regeneration over multiple cycles, surpassing four iterations, without a substantial decline in the efficiency of organic pollutant photodegradation.

The evaluation of ZnS nanostructures' photocatalytic efficacy in removing organic pollutants from industrial wastewater plays a pivotal role. These assessments serve as fundamental benchmarks for initial comparisons and future advancements in diverse ZnS-based photocatalysts. The overarching objective is the continuous improvement of such photocatalysts, enhancing the conversion efficiency of solar energy for applications in green energy production and environmental remediation.

The observed sensitivity of ZnS nanoparticles to microorganisms of notable concern highlights the variability in toxicity among different species. Additional scholarly investigation is crucial to thoroughly examine the exact mechanisms of toxicity, thereby advancing our comprehension of how these nanoparticles affect bacterial sensitivity.

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