



Recent advances in TiO₂/ZnS-based binary and ternary photocatalysts for the degradation of organic pollutants

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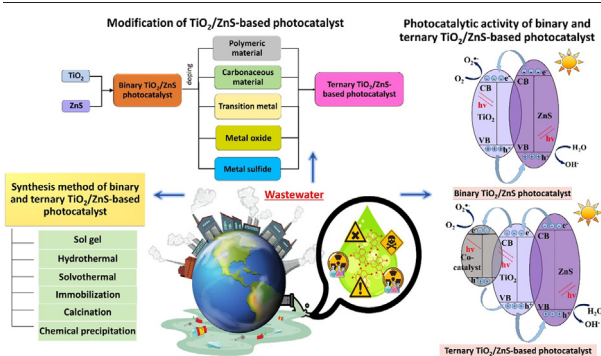
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HIGHLIGHTS

- This review addresses the modifications of TiO₂/ZnS binary and ternary-based photocatalysts
- Modification strategies greatly affect their physicochemical properties and photocatalytic activities
- Ternary TiO₂/ZnS-based photocatalysts have great prospects for the degradation of organic pollutants
- Future research prospects of the TiO₂/ZnS-based photocatalysts have been addressed

GRAPHICAL ABSTRACT



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ABSTRACT

Semiconductor-mediated photocatalysis plays a pivotal role in the elimination of organic pollutants from water systems. Titanium dioxide (TiO₂) and zinc sulphide (ZnS) semiconductors are commonly utilized as photocatalysts in water purification due to their physical and chemical stability and also large band gap. The drawbacks of both semiconductors, nevertheless, prevent them from being used in real and large-scale treatments. Therefore, binary and ternary-based TiO₂/ZnS nanostructured materials may be a promising solution to improve the quantum efficiency, structural, and electrical features of pure TiO₂ and ZnS semiconductors for improved photoefficiency. This review aims to unravel the development of binary TiO₂/ZnS and the modification of ternary photocatalysts (TiO₂/ZnS-X, X = metal, non-metal, and dye sensitization) by various approaches. The engineered TiO₂/ZnS-based ternary nanostructured materials have exhibited exceptional performance to accelerate the degradation of organic pollutants in wastewater. These materials were fabricated by modifying TiO₂/ZnS binary composite and embedding co-catalysts like carbonaceous material, polymeric material, transition metal, metal oxide, and metal. The relationship between the properties of the resulting nanomaterials and their photocatalytic performances has been examined. This review has also placed a special focus on the synthetic routes applied to derive the binary and ternary TiO₂/ZnS composites. Another aim of this review is to scrutinize the factors that influence the performance of binary and ternary-based TiO₂/ZnS composites on the degradation of organic pollutants. Opportunities for further investigation have been also outlined, along with limitations and impediments based on the current findings.

Abbreviations: OP, Organic pollutants; AOP, Advanced oxidation processes; ROS, Reactive oxygen species; PS, Photosensitizer; UV, Ultraviolet; TiO₂, Titanium dioxide; ZnS, Zinc sulphide.

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1. Introduction

In the contemporary world, development and the industrial revolution have become essential. A substantial amount of solid, gas and liquid wastes are disposed of into the environment as a result of extensive development (Singh and Singh, 2017). There is a direct link between environmental pollution and development. Water pollution, greenhouse gas emissions, and other public health-related issues are taking a toll on humankind (Liang et al., 2019). Among these, water, a resource that is essential for all life on Earth, is experiencing an unprecedented crisis. According to United Nations Environment Program (UNEP), over 40 % of the >75,000 water bodies studied by researchers across 89 countries exhibited significant contamination signifying the seriousness of water pollution (Zhongming et al., 2021). Pharmaceuticals, pesticides, detergents, oil, organic dyes, and common industrial organic wastes such as phenols, halogens, cyanide, and aromatics are some of the most frequently found organic pollutants in water. Organic pollutants (OPs) are organic aromatic compounds which may pose major health concerns to people and aquatic ecosystems due to their potentially carcinogenic and persistent nature (Ismail et al., 2019). Conventional biological treatment methods are ineffective due to the resistant nature of OPs. Besides biological treatment, physical methods, for example, adsorption, ultrafiltration, and coagulation have been also employed to remove OPs (Awad et al., 2020). However, these techniques only successfully transfer the pollutants from water to another phase, resulting in secondary contamination that necessitates additional solid waste treatment and adsorbent regeneration, both of which may require additional costs to handle. Therefore, there is a pressing need for efficient, new, and cutting-edge approaches to treating wastewater that is rich in OPs.

Advanced oxidation processes (AOPs) are mainly known to treat drinking water and their application has been extended to the removal of pollutants from wastewater. Among various AOPs, photocatalysis is one of the most popular wastewater treatment techniques as it utilizes solar energy, a renewable type of energy. Titanium dioxide (TiO₂) is one of the semiconductors that is commonly applied in the photocatalytic system to degrade OPs (Al-Rubaiey et al., 2022; Kanakaraju et al., 2022; Mahdi et al., 2021).

TiO₂ semiconductor is predominantly preferred due to its chemical stability, good adsorption characteristic for many contaminants, low cost, non-toxicity, and high photocatalytic efficiency. TiO₂'s large band gap of 3.2 eV however, restricts its absorption to ultraviolet (UV) light, making it ineffective for the exploitation of visible light (Ozturk and Soylu, 2016). Other deficiencies of TiO₂ that needs to be resolved include its agglomeration because of its nanosized particles, quick recombination of electron-hole pairs, and the development of suspension during treatment. In addition, TiO₂, zinc sulphide (ZnS) is also a promising metal sulphide semiconductor. ZnS is nevertheless regarded as an excellent semiconductor despite having a lower photocatalytic efficiency than TiO₂ because of its stability, non-toxicity, fast electron mobility, and rapid production of photogenerated electron-hole pairs (Tahir et al., 2020). Unfortunately, likewise TiO₂, application of ZnS is also limited to UV light ($\lambda < 400$ nm) due to its large band gap of 3.77 eV.

Thus far, various attempts have been made to get beyond the constraints of pristine TiO₂ and ZnS and to improve their photocatalytic performances by loading cocatalysts, defect or band gap engineering, and surface defects (Gupta and Chauhan, 2021; Li et al., 2022; Liu et al., 2022a; Zhang et al., 2021). Up to now, these modifications have resulted in binary (Rajamanickam and Shanthi, 2013; Talebi et al., 2017), ternary (Labiadh et al., 2014; Liu et al., 2015; Mumin et al., 2015) and quaternary-based (Xu et al., 2021) TiO₂/ZnS nanomaterials. Presently, highly advanced Z-scheme systems, two-dimensional (2D) and three-dimensional (3D) nanomaterials which are based on TiO₂ and ZnS are also gaining popularity. Z-scheme systems particularly, are regarded as a suitable strategy to increase the photocatalytic activity of pure photocatalysts (TiO₂ and ZnS) because they allow the reduction and oxidation events to happen on two distinct semiconductors separately and prevent the recombination of photogenerated electrons and holes (Liu et al., 2022b; Liang et al., 2023). A Z-scheme ZnS/CdS-Mn/MoS₂/TiO₂ composite demonstrated remarkable photocatalytic activity and H₂ generation under visible light due to the role of MoS₂ as charge transfer center, the synergistic effect of materials presents and efficient inhibition of the recombination of photogenerated carriers (Feng et al., 2019).