

Research progress on ZnO/MoS₂/rGO ternary photocatalysts

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Abstract: Energy shortages and environmental pollution have become one of the important global issues, and semiconductor photocatalytic technology is considered one of the most effective means to solve these problems. As a new and efficient green material, ZnO has attracted wide attention. ZnO is widely used in the field of photocatalysis due to its non-toxicity, low cost, environmental friendliness, adjustable band gap, high electron density, and chemical stability. However, the recombination of photogenerated charge carriers in ZnO hinders its practical application and lowers the utilization efficiency of visible light. On the other hand, molybdenum disulfide/reduced graphene oxide (MoS2/rGO), as a binary non-precious metal co-catalyst, has a larger specific surface area, suitable band gap width, and visible light response capability compared to a single-phase graphene co-catalyst. Therefore, introducing the MoS₂/rGO co-catalyst into the ZnO system can provide more active sites, reduce the probability of photogenerated charge carrier recombination, and improve the utilization efficiency of visible light. In this review, we summarize the hydrothermal synthesis methods for preparing this highly demanded nanocomposite material, including one-step and stepwise methods. Subsequently, we elaborate on the mechanism of enhancing light absorption and achieving efficient electron-hole separation behavior in the ternary system heterojunction structure during the photocatalytic process. Due to its significant advantages, this ternary system heterojunction structure has been widely applied in the field of photocatalysis, including applications such as pollutant degradation, sterilization, and water splitting.

Keywords: ZnO; MoS₂; graphene; ternary composite materials; photocatalysis

1. Introduction

Since the discovery in 1967 by Fujishima and his colleagues at the University of Tokyo, Japan, that water can be electrolyzed by illuminating a TiO₂ electrode, the application of TiO₂ in the field of photocatalysis has experienced rapid development, and semiconductor photocatalysts have also advanced rapidly as a result [1]. Subsequently, in 1976, Frank and his colleagues successfully applied photocatalytic oxidation technology to the degradation of pollutants in water, achieving breakthrough progress and laying an important theoretical foundation for the application of this technology in wastewater treatment [2]. In 2015, a Japanese company developed a new type of nanophotocatalyst, which is expected to address the increasingly severe water scarcity issue [3]. Since the beginning of the 21st century, energy shortages and environmental pollution have become significant challenges for humanity, with water pollution being particularly prevalent [4]. Therefore, there is an urgent need to explore efficient and clean new energy sources and technologies for treating pollutants. Photocatalysts, as a new and effective green material, have attracted increasing

attention. It is crucial to develop high-performance photocatalysts, with key factors including high light absorption efficiency, a low recombination rate of photogenerated electron-hole pairs, and a large surface area.

In the new generation of photocatalysts, ZnO is widely used in the field of photocatalysis due to its advantages such as non-toxicity, low cost, environmental friendliness, adjustable band gap, high electron density, and chemical stability [5]. Under the illumination of light with energy higher than its band gap, ZnO photocatalysts can undergo photocatalytic reactions, generating strong oxidative radicals and ions, thereby achieving the degradation of organic pollutants [6]. Therefore, ZnO has wide applications in air purification, wastewater treatment, antibacterial materials, and the degradation of organic pollutants. However, ZnO suffers from the recombination of photogenerated charge carriers, resulting in low utilization efficiency of visible light, which hinders the progress of photocatalytic reactions [7]. On the other hand, MoS₂/rGO, as a binary non-precious metal cocatalyst, has a larger specific surface area, a suitable band gap width, and a higher utilization efficiency of visible light compared to simply introducing graphene as a cocatalyst [8]. Therefore, introducing the MoS₂/rGO co-catalyst into the ZnO system can provide more active sites, reduce the recombination probability of photogenerated charge carriers, and enhance the absorption capacity of visible light [9]. ZnO/MoS₂/rGO ternary photocatalyst can effectively improve the solar energy utilization efficiency of semiconductor photocatalysts, and it is one of the important directions to promote the further development of photocatalytic technology (Figure 1) [10]. However, there are still some problems and challenges to be solved in the synthesis and application of ternary systems. Firstly, the controlled synthesis of the ternary system is still in the exploratory stage. In hydrothermal synthesis, the various physical and chemical properties of different components make the influencing factors of structure very complicated, which makes it difficult for researchers to control the formation of morphology while maintaining close contact with heterogeneous structures. In addition, hydrothermal reactions and other precise synthesis methods containing more reaction variables and forms remain to be explored. Secondly, there are still some differences in the catalytic activity of the same system used in the photocatalytic hydrogen evolution reaction, so the heterostructure of the ternary system as the excellent activity source of the photocatalyst still needs further study. This requires more advanced in situ characterization and computational simulation to further elucidate the reaction mechanism and theoretical explanation of catalysis. In order to solve these problems and challenges, it is necessary to systematically summarize the ternary system photocatalysts. Therefore, we summarized the recent progress of ternary system heterostructures as photocatalysts, including synthesis, principle, and application, in order to provide some inspiration and guidance for future researchers.

Herein, this review summarizes the hydrothermal synthesis methods for preparing such high-demand nanocomposite materials, including one-step and stepwise methods. Subsequently, we elaborate on the mechanism of how the heterojunction structure of the ternary system enhances light absorption and achieves efficient electron-hole separation behavior during the photocatalytic process. Due to its significant advantages, this heterojunction structure of the ternary system has been widely applied in the field of photocatalysis, including applications such as pollutant degradation, sterilization, and water splitting. We believe that these studies provide important references for a deeper understanding of the diversity and application potential of ternary composites and open up new possibilities for the development of materials science and energy fields (**Figure 2**).



Figure 1. Number of publications ZnO/MoS₂/rGO ternary photocatalysts according to Web of Science (accessed: 7 March 2024).



Figure 2. The comprehensive overview of ZnO/MoS₂/rGO ternary photocatalysts.

2. Synthesis of the ZnO/MoS₂/rGO ternary system

Due to the complexity of ternary systems, it is often necessary to synthesize heterostructure nanocomposite materials with high specific surface areas under harsh conditions. Therefore, hydrothermal and solvothermal methods are the main synthesis methods. Hydrothermal synthesis refers to the method of forming and growing crystals through chemical reactions and changes in the solubility of substances in a closed heating solution at temperatures and pressures higher than ambient conditions [11]. Typically, this high-temperature and high-pressure environment is achieved using a high-pressure autoclave equipped with a polytetrafluoroethylene (PTFE) container. The conditions of hydrothermal synthesis can be precisely controlled by adjusting internal parameters of the system, such as solute concentration and ratio, pH value, time, pressure, additives, or soft/hard templates, as well as external environmental conditions, such as the method of inputting energy [12]. The solvothermal method is a development of hydrothermal synthesis and typically involves the use of nonaqueous organic reaction systems. Ternary systems require close contact between different materials to form heterostructures and achieve smaller particle sizes for obtaining more reaction sites, making the synthesis of composite materials

challenging. Here, we summarize two different hydrothermal synthesis pathways in order to provide guidance for future researchers in their synthesis endeavors.

2.1. One-step hydrothermal method

Due to the uniform heating environment and highly controllable reaction conditions, the hydrothermal method has become an effective approach for synthesizing high-surface-area nanocomposite materials. In this regard, Guan et al. [13] utilized a one-step hydrothermal method to synthesize heterostructures in a ternary system. They dispersed graphene oxide (GO) in distilled water to prepare a GO solution after subjecting it to ultrasonication for 6 h at 500 W. Then, the GO solution, ZnO, Na₂MoO₄·2H₂O, and thioacetamide were dispersed in distilled water in specific quantities and stirred. Finally, the mixture was heated at 200 °C for 24 h in a high-pressure autoclave. The resulting gray precipitate was washed, dried, and annealed at 300 °C under a nitrogen atmosphere for 2 h, yielding irregular particles with sizes ranging from 40-400 nm. Additionally, some MoS₂ nanoparticles were uniformly dispersed on the surface (Figure 3a). Close contact was formed between ZnO, MoS₂, and reduced graphene oxide (rGO), which facilitated the transfer of electrons from ZnO to RGO and/or MoS₂, thereby delaying the recombination of electron-hole pairs (Figure 3b) [13]. Priyadharsan et al. [14], on the other hand, modified the sulfur source and zinc source to reduce the synthesis temperature and complexity of the reaction system. They first prepared a suspension of reduced graphene oxide (rGO) and sonicated it for 1 h to ensure uniform dispersion. Then, Na₂MoO₄, CH₄N₂S, and Zn(CH₃COO)₂·2H₂O were added to the solution in specific proportions, followed by stirring the solution and heating it at 160 °C for 12 h in a reaction vessel. The resulting sample was washed, dried overnight at 80 °C, and became a ternary nanocomposite material (MZG). MZG consisted of uniformly distributed wurtzite ZnO, flower-like MoS₂ nanospheres, and wrinkled rGO nanosheets. It can be observed that the metal oxide nanoparticles were adsorbed on both sides of the graphene sheets, resulting in a multilayered structure of graphene (Figures 3c and 3d) [14].



Figure 3. (a) SEM image; **(b)** HRTEM image of 0.75 wt%5G95M/ZnO [13]. SEM images of **(c)** and **(d)** MZG nanocomposites [14].

2.2. Stepwise hydrothermal method

To achieve more precise control over the proportions of different components in the ternary system and reduce the limitations of synthesis conditions, researchers have utilized a stepwise hydrothermal method. This approach involves sequentially synthesizing the co-catalyst and photocatalyst to explore the optimal content of different materials for achieving synergistic effects while ensuring close contact between the heterostructures. Ugur et al. [15] employed a multi-step hydrothermal method to precisely control the proportion of the co-catalyst in the sample, aiming to achieve positive synergistic effects in the ternary system. Firstly, they used Na₂MoO₄·2H₂O, CH₄N₂S, and graphene oxide (GO) as precursors to synthesize MoS₂rGO (MG) through hydrothermal synthesis, adjusting the content of rGO to achieve different hybridization effects. Subsequently, the obtained MG composite was dispersed in a 100-mL solution containing 30 mL of ethanol and 70 mL of deionized water, and 300 mg of ZnO dispersed in 100 mL of deionized water was added dropwise. The mixture was stirred for 2 h at room temperature. The resulting mixture was then heated in a high-pressure autoclave at 180 °C for 10 h, followed by cooling to room temperature, washing, and drying, resulting in the successful synthesis of the sample (Figure 4a) [15]. Kumar et al. [16], on the other hand, used Na₂MoO₄·2H₂O, GO, and L-cysteine as precursors. The precursors were subjected to a high-pressure autoclave at 180 °C for 24 h. The resulting product was washed and dried overnight at 80 °C to obtain MoS₂-rGO hybrid. Subsequently, the hybrid material was dispersed in deionized water, and a solution containing Zn(CH3COO)2·2H2O and NaOH was added to form a homogeneous solution. The solution was then transferred to a high-pressure autoclave and treated at 160 °C for 2 h. After washing and drying, the desired product was obtained. This method allows for the control of the MoS2-rGO hybrid content to optimize the heterostructure (Figure 4b) [16]. Li et al. [17] proposed a microwaveassisted method to synthesize the MoS₂-rGO component in the ternary system. They added varying amounts of GO to a solution of phosphomolybdic acid hydrate and adjusted the pH to 7 using a NaOH solution. Then, they added a thioacetamide solution and stirred for 10 min to generate a homogeneous dispersion. Subsequently, the mixture was heated at 150 °C for 10 min under microwave irradiation with a power of 150 W using an automated focusing microwave system. After washing and drying the resulting precipitate, the sample was obtained [17].



Figure 4. (A) XRD images of ZnO/MG hybrids [15]; **(B)** XRD patterns of a: ZnO NP, b: ZMG0.5, c: ZMG1 and d: ZMG2 [16].

In conclusion, the current synthesis of ternary systems primarily relies on relatively simple hydrothermal methods. However, there is a lack of in-depth exploration and understanding of additional reaction conditions (such as external fields, templates, etc.) and synthesis mechanisms.

3. Photocatalytic applications of ZnO/MoS₂/rGO ternary system

For a long time, the photocatalytic activity of semiconductors has been limited by issues such as low efficiency, narrow light absorption range, and rapid recombination of photogenerated electron-hole pairs [18–20]. Combining widebandgap and narrow-bandgap semiconductors to form heterostructures with band offset has been proven to be an effective strategy for improvement [21]. In this research context, researchers have paid significant attention to the heterostructure of a ternary system composed of wide-bandgap ZnO, narrow-bandgap MoS₂, and zerobandgap graphene with a low Fermi level [22–24]. Due to the difference in the conduction band (CB) positions between ZnO and MoS₂, photogenerated electrons can thermodynamically transfer from ZnO to MoS₂, thereby slowing down the recombination process of electron-hole pairs (**Figure 5**). At the same time, rGO in graphene, with its two-dimensional sp²-hybridized conjugated structure, exhibits favorable band potential and Fermi-level positions. It can act as an electron reservoir, receiving and transferring electrons from active sites in photocatalytic reactions [25].



Figure 5. Schematic illustration of the potential and band positions for the ZnO, MoS₂ and rGO [13].

rGO also possesses excellent physicochemical properties, which can alleviate the aggregation issue of MoS_2 and ensure close contact between semiconductors, thus forming a stable heterostructure [26]. Furthermore, some literature suggests that doping MoS_2 and rGO as co-catalysts into ZnO can effectively adjust the band positions of the heterostructure, enhance visible light absorption, and improve overall light absorption capacity. Based on these findings, we have summarized some understanding of the heterostructure of the ternary system in overcoming challenges in semiconductor photocatalysis and outlined the research progress of the ternary system widely applied in photocatalytic hydrogen evolution, pollutant degradation, and antibacterial applications.

As an efficient photocatalyst that is metal-free, non-toxic, and low-cost, ZnO is limited by its wide band gap, which can only be excited by ultraviolet (UV) radiation

[27–29]. However, UV radiation accounts for only about 5% of the solar spectrum, while the visible light region accounts for approximately 43%. This significantly limits the energy utilization efficiency of ZnO [30,31]. Therefore, it is necessary to broaden the light absorption range of ZnO to the visible light region and enhance its light absorption/capturing capability. In this regard, Kumar et al. proposed the ZnO-MoS₂rGO heterostructure, which enhances light capture in both the UV and visible light regions, thereby generating more photo-induced charge carriers. Through diffuse reflectance spectroscopy (DRS) analysis in the range of 200-800 nm, they found that the light absorption capacity of the heterostructure increases with increasing MoS₂-RGO content (Figure 6). This is attributed to the absorption characteristics of MoS_2 in the wavelength range of 200-800 nm, and the synergistic effect of MoS₂-rGO leads to a redshift in the absorption spectrum of the heterostructure, enabling better utilization of the visible light region. For samples with different doping levels, they explained the variation in the bandgap as a result of chemical bonding at specific sites between the semiconductor and GO, leading to charge delocalization and optimizing the optical properties of the heterostructure [16,32].



Figure 6. DRS of GO, ZnO NP, MoS₂-RGO, ZMG0.5, ZMG1 and ZMG2 [16].

In semiconductor materials used for photocatalysis, the photogenerated electrons in the CB exist in metastable states and eventually recombine with holes in the VB. The rapid recombination of electron-hole pairs shortens the lifetime of charge carriers, resulting in lower photocatalytic activity [33]. Extending the charge transfer pathway is one effective way to enhance the material's capability for photocarrier separation. Ternary systems composed of semiconductors with different band gaps and rGO demonstrate significant potential in this regard [34]. Regarding the application of MoS2-rGO/ZnO in photocatalytic hydrogen evolution, Guan et al. proposed the reasons behind the high hydrogen evolution activity of the ternary system, attributing it to the positive synergistic effect between MoS₂ and rGO, where rGO functions as both a co-catalyst for hydrogen evolution and a powerful pathway for electron transfer (Figure 7a). Through characterization techniques such as UV-vis absorption spectroscopy (Figure 7d), nitrogen adsorption-desorption analysis, photoluminescence (PL) spectroscopy (Figure 7e), and photocurrent response measurements (Figure 7b), they ruled out other factors influencing the hydrogen evolution activity and demonstrated that rGO accelerates the transfer of electrons from ZnO to MoS₂, improving electron transport. This impedes the recombination of

electron-hole pairs in the material, thereby enhancing the release activity of H₂. Additionally, they proposed a mechanism to explain the hydrogen evolution process in the ternary system and provided insights for the design of other multicomponent photocatalysts [13]. Regarding the photocharge enhancement and charge separation capability in the ternary system, Kumar et al. [16] provided another insight (Figure 7c). They noted that in the process of photocatalytic hydrogen evolution, the presence of catalyst dispersed in the electrolyte (S^{2-} and SO_3^{2-}) enhances the hydrogen evolution rate (Figure 7f), with the optimal sample exhibiting a performance of 28.616 mmol $h^{-1}g_{cat}^{-1}$ under sunlight irradiation. They attributed this to the in-situ generation of ZnS, which improves the interface charge transfer between the co-catalyst MoS₂ and rGO. Furthermore, rGO provides a large number of active sites available for photocatalytic reactions. Through characterization experiments such as scanning electron microscopy, transmission electron microscopy, X-ray diffraction, and energydispersive X-ray spectroscopy, they proved the presence of ZnS and indicated that the generation of ZnS results in extended absorption in the visible light region. Additionally, they suggested that the CB of ZnS has a lower potential than that of ZnO, while the VB of ZnO has a positive potential relative to that of ZnS [35,36]. The more negative CB potential of ZnS allows electrons to transfer from the CB of ZnS to the CB of ZnO, while holes transfer from the VB of ZnO to the VB of ZnS. As a result, the ZnS-ZnO heterostructure facilitates the effective separation of photogenerated charge carriers at the interface. Furthermore, rGO acts as an electron acceptor and shuttle, with its high charge transfer mobility extending the lifetime of photogenerated charge carriers [37].



Figure 7. (a) mechanism of H₂ evolution process in the MG/ZnO composite under irradiation; **(b)** transient photocurrent responses; **(c)** scheme of ZnO-MoS₂-rGO ternary nanocomposites; **(d)** UV-vis absorption spectra; **(e)** the PL spectrum of pure ZnO, 0.75 wt% MoS₂/ZnO, 0.75 wt% rGO/ZnO and 0.75 wt% 5G95M/ZnO samples [13]; **(f)** proposed mechanism for enhanced electron transfer across the ZnS-ZnO-MoS₂-rGO hetero-junction under sunlight irradiation for photocatalytic H₂ generation with Na₂S-Na₂SO₃ as a sacrificial reagent [37].



Figure 8. (a) reusability of rGO/ZnO/MoS₂ nanocomposite in optimal condition for degradation process of aniline during the five cycles [38]; (b) photocatalytic degradation of BR18 dye for 25ZnO/75MG1 and 75ZnO/25MG1 [15]; (c) zone of inhibition tests for WFG nanocomposites materials towards gram-negative *E. coli* bacteria and gram-positive *S. aureus* bacteria; (d) photocatalytic mechanism scheme of the MZG nanocomposite [14].

The enhanced light absorption capacity, photocarrier separation ability, and prolonged carrier lifetime greatly expand the application range of ternary systems in photocatalytic applications. Ghasemipour et al. [38] applied rGO/ZnO/MoS₂ ternary nanocomposites to the photocatalytic degradation of aniline in aqueous solutions and investigated the effects of operational variables such as solution pH, catalyst dosage, and initial aniline concentration on achieving maximum degradation efficiency. They found that under conditions of pH = 4, catalyst dosage of 0.7 g L^{-1} , aniline concentration of 80 ppm, and light intensity of 100 W, complete degradation of aniline was observed. Based on the results of scavenger experiments, hydroxyl radicals were identified as the main active species in the photocatalytic reaction. Additionally, due to the synergistic effects between the components in the ternary system, the catalyst exhibited excellent reusability and stability even after five consecutive uses (Figure **8a**). This study demonstrates the tremendous potential of $rGO/ZnO/MoS_2$ in treating various organic pollutants in wastewater. Priyadharsan et al. [38] proposed that MoS₂-ZnO-reduced graphene oxide (MZG) nanocomposites exhibit high antibacterial activity against Escherichia coli (E. coli) and Staphylococcus aureus (S. aureus) (Figure 8d). They investigated the antibacterial activity of MZG nanocomposites against these two pathogenic bacteria using the well diffusion method on Mueller-Hinton agar plates (Figure 8c). The results demonstrated that the antibacterial activity of MZG nanocomposites was positively correlated with the dosage. At higher concentrations (100 μ g mL⁻¹), bacterial growth was completely inhibited. The biodeactivation mechanism occurred through the production of abundant surface oxygen, leading to bacterial membrane rupture and ultimately killing the pathogens. This study

highlights the potential application of ternary materials as effective antibacterial agents [14,39]. Ugur et al. [15] synthesized a ternary hybrid nanostructure composed of ZnO nanorods and MG co-catalyst and applied it to the degradation of the water pollutant BR18 dye commonly found in the textile industry. Under the conditions of 25ZnO/75MG1 heterostructure, 100% dye degradation could be achieved within 180 min (**Figure 8b**). When the content of GO in the co-catalyst increased to 5%, 25ZnO/75MG2 achieved complete degradation of the dye solution within the first 30 min. They attributed this excellent photocatalytic performance to the positive synergistic effect of the MoS₂-rGO co-catalyst and highlighted the effective role of GO content in accelerating charge separation and electron transfer characteristics [15].

4. Conclusions

The ZnO/MoS₂/rGO ternary system heterostructure is a highly promising photocatalyst that benefits from the synergistic interaction between the catalyst and co-catalyst. This system exhibits significant advantages in terms of solar light absorption capacity and range, specific surface area, and efficiency of photogenerated electron-hole separation. This review summarizes the hydrothermal synthesis methods for preparing such high-demand nanocomposite materials, including one-step and stepwise methods. Subsequently, we elaborate on the mechanism of how the heterostructure of the ternary system enhances light absorption and achieves efficient electron-hole separation behavior during the photocatalytic process. Due to its tremendous advantages, this ternary system heterostructure has been widely applied in the field of photocatalysis, including applications such as pollutant degradation, sterilization, and water splitting (**Table 1**).

Material	Synthesis	Catalytic performance	Ref.
ZMG1	Stepwise hydrothermal method	The degradation of MB dye and carbendazim under natural sunlight irradiation: 98% after 60 min	[16]
0.5 wt%MoS2/ZnO	One-step hydrothermal method	Photocatalytic H ₂ evolution: 98.1 μ mol g ⁻¹ h ⁻¹	[13]
ZMG4	Stepwise hydrothermal method	Photocatalytic H ₂ evolution: 28.616 mmol h^{-1} g ⁻¹	[37]
RGO 10%/ZnO 20%/MoS ₂	One-step hydrothermal method	In real wastewater, the COD and TOC ratios decreased to zero and 7%, respectively after 440 min under the operational conditions.	[38]
MZG	One-step hydrothermal method	The growth of <i>E. coli</i> and <i>S. aureus</i> in Mueller Hinton agar in the concentration of 100 μ g/mL was completely declined	[14]
25ZnO/75MG1	Stepwise hydrothermal method	100% degradation of BR18 dye for 180 min	[15]

 Table 1. Synthesis methods for various heterostructures.

5. Perspective

Despite the enormous potential of the ZnO/MoS₂/rGO ternary system as an efficient photocatalyst, it still faces significant challenges in both fundamental and practical aspects:

 The content ratio of different components in the ternary system needs to be optimized for specific applications (Figure 9). A high co-catalyst content may lead to light shielding effects, reducing the number of active sites in ZnO and hindering the excitation of photogenerated charge carriers. On the other hand, a low co-catalyst content may be insufficient to effectively prevent particle aggregation and achieve efficient charge separation.

- 2) The utilization of photocatalytic active sites is influenced by factors such as the size, morphology, pore structure, phase, and impurities of the highly efficient catalyst nanostructures. Therefore, the development of more efficient and diverse synthesis methods is crucial to synthesizing phases with high photocatalytic activity and achieving precise control.
- 3) Further optimization of the co-catalyst is still needed. Strategies such as heteroatom doping and introducing vacancies can improve the electron state density of the co-catalyst, leading to enhanced electron mobility and charge separation efficiency. Further exploration is required in this aspect.
- 4) A deeper understanding of the relationship between composition, structure, and performance requires a collaborative effort between theoretical calculations and experimental validation.



Figure 9. A volcano-type relationship between the loading amount of a cocatalyst and the photocatalytic activity of the cocatalyst-loaded semiconductor photocatalyst [21].

Addressing these challenges will require further research and exploration to achieve the efficient application of $ZnO/MoS_2/rGO$ ternary system photocatalysts.

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