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The band structure control of visible-light-driven rGO/ZnS-MoS_2 for excellent photocatalytic degradation performance and long-term stability

Xiufen Hu[a], Fang Deng[a,*], Weiya Huang[b], Guisheng Zeng[a], Xubiao Luo[a,*], Dionysios D. Dionysiou[c]

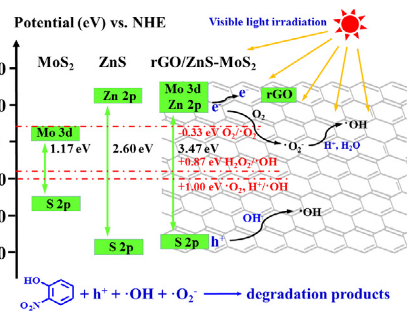
[a] Key Laboratory of Jiangxi Province for Persistent Pollutants Control and Resources Recycle, Nanchang Hangkong University, Nanchang 330063, China
[b] School of Metallurgy and Chemical Engineering, Jiangxi University of Science and Technology, Ganzhou 341000, China
[c] Environmental Engineering and Science Program, Department of Biomedical, Chemical and Environmental Engineering (DBCEE), University of Cincinnati, Cincinnati OH 45221-0012, USA

HIGHLIGHTS

- rGO/ZnS-MoS_2 was synthesized by solvent thermal method.
- 11% rGO/ZnS-MoS_2 shows the highest visible-light photocatalytic activity.
- rGO/ZnS-MoS_2 is especially efficacious in real wastewater treatment.
- rGO/ZnS-MoS_2 maintain long-term stability.

GRAPHICAL ABSTRACT

The band structure of rGO/ZnS-MoS_2 catalyst.



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ABSTRACT

ZnS-MoS_2 solid solution anchored on reduced graphene oxide sheet (rGO/ZnS-MoS_2) was explored as novel visible-light-driven photocatalysts, and synthesized by solvent thermal method. The light absorption intensity of rGO/ZnS-MoS_2 was greatly strengthened, and rGO/ZnS-MoS_2 possess modulated continuous band gaps from 3.47 to 3.56 eV by changing the Zn/Mo ratios and rGO content. Their photocatalytic activities for 2-nitrophenol degradation are dependent on the chemical composition, and the optimal 11% rGO/ZnS-MoS_2 possessed the highest photocatalytic performance, which could be attributed to the most efficient charge separation, the largest specific area, and its optimized band structure. Moreover, 11% rGO/ZnS-MoS_2 can effectively treat real industrial effluent with 74.05% COD removal, and maintain long-term stability without obvious decline after five use cycle.

1. Introduction

The rapid development of industry has brought about serious pollution of industrial wastewater [1]. The characteristics of industrial wastewater usually include complex components, high concentration of refractory organic pollutants, high chromaticity and poor biodegradability [2]. The harmful pollutants in industrial wastewater have negative impact on environmental quality, ecosystem safety and human health [3,4]. Therefore, how to effectively deal with industrial wastewater to meet wastewater discharge standard is an important goal of environmental protection.

At present, the methods for industrial wastewater treatment include

* Corresponding authors.
E-mail addresses: dengfang40030@126.com (F. Deng), luoxubiao@126.com (X. Luo).

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adsorption, membrane treatment technology, electrochemical treatment, activated sludge process, ozonation, ion exchange and photocatalytic degradation [5–12]. Among them, photocatalytic degradation has been considered as a promising and sustainable technology for wastewater treatment due to its advantages of simple processing equipment, high efficiency, easy control and no secondary pollution [13–16]. Zinc sulfide (ZnS) is a typical II-VI semiconductor, and has received considerable concern due to its excellent properties such as strong oxidation ability and low secondary pollution [17,18]. However, ZnS is only active in UV-light region, and its photocatalytic activity is not high enough due to the wide band gap (3.6 eV) and fast recombination of photo-generated electrons and holes [19,20]. The fabrication of heterojunction with distinct narrow band gap semiconductors is an efficient and popular method to broaden visible-light absorption range and enhance photocatalytic properties [21,22]. MoS_2 has broad application prospects as an emerging photocatalyst due to narrow band gap, complex edge structure, large surface area and highly unsaturated property [23], and some efforts were made to facilitate the formation of ZnS-MoS_2 heterojunctions to inhibit recombination of photo-generated electrons and holes, and improve the photocatalytic activities [24]. However, the heterojunctions always suffer from poor lattice matching and band structure [25]. The solid solution of semiconductors is considered as an efficient way to avoid interface stress originated from the lattice mismatch and optimize the band structure matching by tuning lattice constant and band structure [26]. Our research group has developed a series of ZnS-MoS_2 solid solution, and the photocatalytic activities of ZnS-MoS_2 solid solution are much higher than those of pure ZnS and pure MoS_2, but the photocatalytic activity of ZnS-MoS_2 is still not satisfactory due to poor electrical conductivity (see Supporting information, Fig. S1).

Reduced graphene oxide (rGO) exhibits superior electron mobility and excellent electrical conductivity, and is widely used as a good matrix for many semiconductors to promote the separation of charge carriers and further enhance the photocatalytic activities [27–29]. Combined the advantages of ZnS-MoS_2 solid solution and the excellent properties of rGO, we attempted to fabricate a novel ternary rGO/ZnS-MoS_2 which was expected to facilitate charge separation and stability.

In this study, ternary rGO/ZnS-MoS_2 was fabricated by a one-step solvent thermal process, and the different rGO amount had obvious influence on the physicochemical properties and visible-light photocatalytic activity of rGO/ZnS-MoS_2. Close contact interface and tunable band structure play synergetic role in enhancing charge separation, leading to enhanced photocatalytic activity of rGO/ZnS-MoS_2. Moreover, rGO/ZnS-MoS_2 can effectively treat real pharmaceutical industry wastewater with 74.05% chemical oxygen demand (COD) removal efficiency, and shows excellent stability without obvious decreases in photocatalytic activity after five degradation cycles.

2. Experimental section

2.1. Chemicals

Sodium molybdenum oxide dihydrate ($Na_2MoO_4 \cdot 2H_2O$) and thioacetamide (TAA) were purchased from J&K, Shanghai. Zinc acetate dihydrate ($Zn(Ac)_2$) and 2-nitrophenol (2NP) were purchased from Aladdin Chemistry Co., Ltd. (Shanghai, China). P-Benzoquinone (BQ) was supplied by Shanghai Crystal Pure Reagent Co., Ltd. (Shanghai, China). Triethanolamine (TEOA) was acquired from Shanghai Chemical Reagent Co., Ltd. (Shanghai, China). Sulphuric acid (H_2SO_4), potassium dichromate ($K_2Cr_2O_7$), silver sulfate (Ag_2SO_4), anhydrous ethanol, *iso*-propyl alcohol (IPA) were provided by Shantou Xilong Chemical Co., Ltd. (Shantou, China). All chemicals were used as received. Pharmaceutical wastewater was obtained from Jiangxi Chemedir Biopharm-tech. Co., Ltd. (Jiujiang, China). Deionized water was purified using a Milli-Q water system (Bedford, USA).

2.2. Synthesis of rGO/ZnS-MoS_2

GO was synthesized by referring to modified Hummers method [30]. rGO/ZnS-MoS_2 was facilely synthesized via solvent thermal method. 6 mmol $Zn(Ac)_2$, 0.2 mmol $Na_2MoO_4 \cdot 2H_2O$, and 13.3 mmol TAA were added in 40 mL ethanol under magnetic stirring until a uniform solution was formed, then GO with a certain mass fraction of x % (x = 5, 8, 11, 14) was added into 10 mL ethanol to form a suspension solution and interfused into above mixture solution. The final suspension was transferred to 100 mL Teflon-lined stainless steel autoclave and heated at 210 °C for 24 h. After the reaction, a dark gray precipitate was obtained, washed with deionized water and ethanol several times, and finally dried at 60 °C in vacuum.

2.3. Characterization

X-ray diffraction (XRD) with Cu-Kα radiation (λ = 0.154056 nm) was used to characterize the crystal phase of the different samples at 40 kV and 40 mA in the 2θ range of 5° to 80°. Scanning electron microscopy (SEM, Shimadzu, Japan) and transmission electron microscopy (TEM, JEOL, Japan) was used to observe the morphology of photocatalysts. Raman spectra were recorded using microscopic confocal Raman spectrometer (Renishaw, INVIA) at 532 nm laser excitation. The chemical state of elements was analyzed by an AXIS Supra X-ray photoelectron spectrometry (Shimadzu, Japan). UV–Vis diffuse reflectance spectroscopy was measured using U-3900H UV–Vis spectrophotometer (Hitachi, Japan) using $BaSO_4$ as a reference. The BET surface area and pore-size distribution were analyzed using a GEMINI VII 2390 surface area and porosity analyzer (Micromeritics, USA). The photoluminescence (PL) spectra were measured using F-7000 fluorescence spectrophotometer (Hitachi, Japan) at 380 nm excitation wavelength. The chemical oxygen demand (COD) of real pharmaceutical industry wastewater was analyzed using a DR1010 COD determinator (Hach, USA). The thermal stability was studied by TG-209 thermogravimetric Analyzer (Netzsch, Germany) in the temperature range from 50 to 700 °C with an increment of 10 $°C \cdot min^{-1}$ in the nitrogen atmosphere with gas flow rate of 100 $mL \cdot min^{-1}$.

2.4. Photocatalytic experiments

The photocatalytic activities of rGO/ZnS-MoS_2 were investigated by monitoring the photodegradation efficiency of 2NP under the irradiation of 300 W xenon lamp (PLS-SXE300, Beijing Trusttech Co., Ltd., China) with a 420 nm cut-off filter. 50 mg photocatalysts were added into 100 mL 10 mg/L 2NP solution under magnetic stirring, maintained dark reaction for 40 min to achieve adsorption-desorption equilibrium before light exposure. After visible-light irradiation, 3 mL of suspension was withdrawn with a syringe at time intervals of 20 min, and immediately was filtered. The filtrate was analyzed using a 754 UV–vis spectrometer at a wavelength of 274 nm.

2.5. The practical application of rGO/ZnS-MoS_2 catalyst in the treatment of real pharmaceutical wastewater

The sampling process for COD removal of real pharmaceutical wastewater was similar to the above photocatalytic experiments. The COD of real pharmaceutical wastewater was measured according to the reference [31].

2.6. Free radicals trapping experiments

Hydroxyl radical ($^{\cdot}OH$), superoxide radical ($^{\cdot}O_2^{-}$) and hole (h^+) were detected by adding IPA, BQ and TEOA to photocatalytic system, respectively. The experiment procedure was identical to the above photocatalytic experiments.