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Novel WS_2/ZnS composite with high performance of the adsorption and photocatalysis

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ABSTRACT

Both adsorption and photodegradation are effective methods to treat organic pollutants in water. Adsorbent materials, such as activated carbon, are generally disposable and difficult to reuse. By contrast, photocatalysts can be reused to treat organic pollutants in water. However, the slow degradation rate of photocatalysts cannot meet the emergency treatment of contaminants. Therefore, we proposed a novel WS_2/ZnS composite with ZnS as the catalyst, and WS_2 as the adsorption, both of which were sulfide. The WS_2/ZnS composite was synthesized by a two-part hydrothermal method. The crystal structure, surface morphology and pore size of WS_2/ZnS were analyzed by X-ray diffraction, scanning electron microscopy and Brunauer–Emmett–Teller. The experimental results show that the WS_2/ZnS composite material was successfully synthesized and had a rough surface and a high specific surface area (40.6 m^2/g). Then, the photocatalytic performance of WS_2/ZnS was analyzed. The results showed that the WS_2/ZnS composite material could effectively adsorb and catalyze 96% organic materials within 20 min. Repeated experiments have proven that WS_2/ZnS has excellent recyclable properties, and the catalytic performance of the WS_2/ZnS catalyst was still similar to that of the first use after 5 uses. In addition, WS_2/ZnS also has excellent treatment ability for complex organic pollutants in water environment that simulates actual dye wastewater. The results show that the WS_2/ZnS composite was a fast, efficient and reusable adsorption-catalyst that can treat emergency pollution immediately.

Keywords: Adsorption; Photocatalysis; WS_2/ZnS; Water pollution

1. Introduction

Environmental pollution is one of the most serious problems presently faced on a global scale. The increase of the population and the unabated release of residential and industrial wastewater have resulted in environmental problems such as global warming and abnormal climatic changes [1]. All these pollutants have prompted the development of environmental remediation technologies. Photocatalysis which is a kind of inexhaustibly abundant, clean [2,3], non-hazardous, and economically viable technology, is a major advance in this direction [4–6]. Semiconductor materials with potentially broad designs are prospective photocatalysts for the complete elimination of toxic chemicals [7]. ZnS is an important II–VI group semiconductor material. For the rapid generation of electron hole pairs by photoexcitation and the highly negative reduction potentials of excited electrons [8], the photocatalytic performance of ZnS has been intensively studied. ZnS can be used as an effective catalyst for splitting water to produce H_2 [9–11] and for the photoreduction of CO_2 [12,13]. Another important application of ZnS is as a promising photocatalyst for the

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photocatalytic degradation of environmental pollutants [14]. ZnS has been used for the photocatalytic degradation of organic pollutants such as methylene blue [15], methyl orange dyes [16], p-nitrophenol [17,18], and halogenated benzene derivatives [19] in wastewater treatment. Organic pollutants could be oxidized into CO_2 and H_2O under light irradiation on the surface of ZnS, bringing no more other pollution. However, the application of ZnS in photocatalysis was limited to its efficiency. It would take hours to eliminate the organic pollutants completely. Therefore, photocatalysis generally cannot treat emergency pollution immediately. Conversely, adsorbents such as activated carbon [20,21], natural clay [22], and nanosized materials can deal with pollution rapidly due to their higher specific surface area. However, the problem of pollution could not be solved fundamentally. Pollution could only be absorbed to the surface of adsorbents rather than degraded to an inorganic state by photocatalysis. Compared with ZnS, WS_2 as a sulfide has a larger specific surface area and stronger adsorption performance [23]. In addition, the unique band position of WS_2 could also play a role in separating carriers. This will be beneficial to the improvement of photocatalytic performance.

Here, we designed a new composite material, that combines WS_2 with high adsorption performance and ZnS with high photocatalytic performance. The rhodamine B degradation performance, repeatability test, a variety of dye degradation experiments of the WS_2/ZnS catalyst were investigated. The results showed that a novel catalyst (WS_2/ZnS) with high efficiency and green treatment of pollutants in water was obtained.

2. Experimental section

2.1. Catalyst preparation

WS_2 was obtained by the following method: 1.19 g tungsten chloride and 1.13 g thioacetamide were dissolved in 80 mL deionized water. The mixed solution was fully stirred and transferred to a hydrothermal reactor. The hydrothermal reactor was placed in an oven at 235°C for 24 h. Then, the samples were washed repeatedly with deionized water and alcohol and centrifuged and dried at 60°C in a vacuum oven.

The WS_2/ZnS catalyst was obtained by the following step: 0.22 g zinc acetate and 0.30 g thiourea were weighed and dissolved in deionized water and ethylenediamine with a volume ratio of 1:1. The solution was stirred thoroughly on a magnetic stirrer to completely dissolve. Then, 0.3 g WS_2 prepared according to the above method was added to the above solvent and stirred to fully mix it. The solvent was put into a high temperature reaction kettle and placed in a drying oven at 200°C for 12 h. The samples were washed repeatedly with deionized water and alcohol, and then, centrifuged and dried at 60°C in a vacuum oven.

To compare the performance of WS_2/ZnS catalysts, pure ZnS materials were also prepared by the solvothermal method. A total of 1.83 g zinc acetate and 1.34 g thiourea were weighed and dissolved in 50 mL deionized water. The solution was stirred thoroughly on a magnetic stirrer to completely dissolve. The solvent was put into a high temperature reaction kettle and placed in a drying oven at 200°C for 12 h. The samples were washed repeatedly with deionized water and alcohol. Then, the ZnS material was obtained by centrifuging and drying at 60°C in a vacuum oven.

2.2. Characterization of catalysts

The crystal structure of the as-prepared WS_2/ZnS samples were characterized by X-ray diffraction (XRD, Rigaku D/max-2500, Japan). The surface topographies were obtained with scanning electron microscopy (SEM, JSM-6010LA, Japan). The specific surface area of the sample was measured by the specific surface area and pore size analyzer Brunauer–Emmett–Teller (BET, BK123F, China). The optical properties of the samples were tested by an assembled photoluminescence system.

2.3. Photocatalytic properties test

WS_2/ZnS prepared by the above step was dispersed in 100 mL of 10 mg/L rhodamine B solution. The mixed solution was stirred for 20 min in the dark to attain adsorption–desorption equilibrium. Then the photo-degradation experiments were performed under UV-visible light illumination (Philips HPA 500S, 500 W). The liquid level was 50 cm away from the ultraviolet light illumination. The rhodamine B solutions were then centrifuged to investigate the concentration by a UV-Vis spectrometer (UV-2501, Shimadzu) every 20 min. In addition, we simulated a complex water environment similar to actual water pollution by mixing three dyes (rhodamine B, methylene blue, crystal violet) in the same proportions so that the dye concentration was 10 mg/L. The ability of the WS_2/ZnS composite to treat organic pollutants in a complex water environment was tested according to the above photocatalytic experiment process test. All photocatalytic experiments were repeated three times for each sample.

3. Results and discussion

3.1. Characterization of crystal structure and surface morphology

XRD analysis was used to investigate the material composition of WS_2/ZnS. As shown in Fig. 1a, the blue and red patterns are the XRD spectra of pure WS_2 and ZnS prepared by the solvothermal method. All the diffraction peaks can correspond to PDF cards (No. 08-0237 and No. 36-1450). The black pattern can be attributed to the XRD pattern of the WS_2/ZnS composite material. The XRD diffraction peaks contain the basic characteristic peaks of WS_2 and ZnS. The results show that the WS_2/ZnS composite material could be obtained by the hydrothermal method. To study the morphology of the composites, the ZnS, WS_2 and WS_2/ZnS composites were characterized by SEM (Fig. 1b–d). Fig. 1b shows the SEM of ZnS prepared by the hydrothermal method. ZnS appears to be a 3–6 μm sphere with a smooth surface. Fig. 1c shows that the WS_2 materials prepared by us are hollow spheres with a diameter of less than 1 μm. It can be inferred that WS_2 had a large contact area with pollutants and excellent adsorption performance. Fig. 1d shows the SEM image of WS_2/ZnS, and the size of the composite material

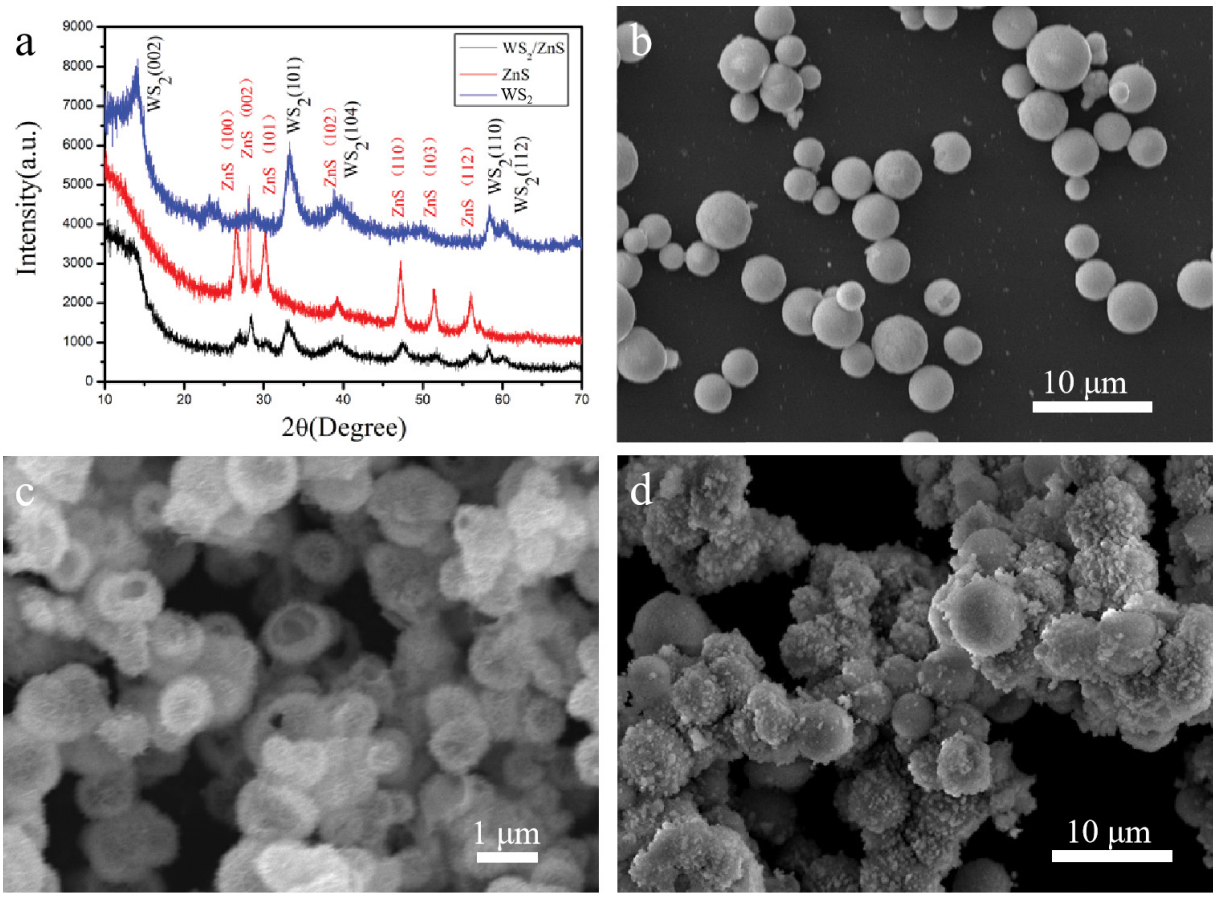

Fig. 1. (a) XRD spectra of WS_2, ZnS, and WS_2/ZnS composite materials, (b) SEM image of ZnS prepared by solvothermal method, (c) SEM image of WS_2 and (d) SEM image of WS_2/ZnS.

is basically the same as that of ZnS. However, the surface morphology of WS_2/ZnS is rough. By comprehensive comparison of three XRD patterns and SEM images, we can infer that the main sphere of the WS_2/ZnS composite was mainly the ZnS material, while the rough particles on the surface were WS_2.

3.2. Analysis of specific surface area

The BET of the three materials were tested to analyze the surface adsorption capacity. The experiment shows that the BET of ZnS was small, only 15.2 m^2/g. While the specific surface area of WS_2 was the largest at 74.0 m^2/g. The area of the WS_2/ZnS composite was in the middle, approximately 40.6 m^2/g. The adsorption–desorption curve of WS_2/ZnS composite materials is shown in Fig. 2a, which belongs to the type IV isothermal curve. When P/P_0 is less than 0.8, the isothermal curve shows a linear relationship, which indicates that the adsorption was caused by the adsorption of monolayer molecules within the range of 0~0.8 relative pressure. When the relative pressure ratio is greater than 0.5, the adsorption curve increases obviously, indicating that there was multi-molecular layer adsorption or capillary condensation in the material. Fig. 2b shows the pore-size distribution of WS_2/ZnS. The two pore size peaks indicate that the pore sizes of the composite materials are mainly 2.2 nm micropores and 57.9 nm mesopores. These results suggest that the material contained micropores and mesopores which can promote the surface adsorption of organic molecules.

3.3. Photocatalytic performance test

We tested the photocatalytic properties of the three materials (WS_2, ZnS and WS_2/ZnS), which are shown in Fig. 3a. ZnS had good photocatalytic performance. However, the rate of degradation was not particularly fast. It took 140 min to degrade rhodamine B to the original concentration of 53%. The adsorption performance of pure WS_2 had a good behavior, which could absorb large amounts of pollutants (90%) before illumination. However the photocatalytic efficiency of WS_2 was poor. The WS_2/ZnS composite material prepared by us had the advantages of both WS_2 and ZnS, which could dispose of 96% organic pollutants in water in 20 min. This indicates that the speed of WS_2/ZnS treatment of organic pollutants is approximately 3–6 times that of traditional photocatalysts, such as Fe_3O_4/TiO_2 [24], and RGO/Cu [25]. It is suggested that WS_2/ZnS composite materials can be effectively applied in the treatment of emergent organic pollutants. Although there was no significant change in the rhodamine B concentration after illumination for 20 min, we believe that ZnS would degrade rhodamine

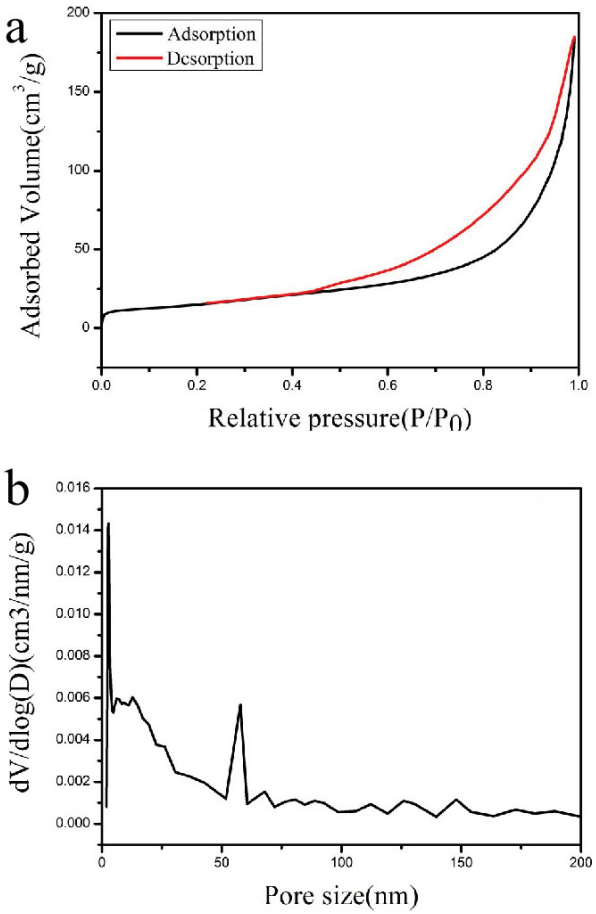

Fig. 2. (a) Adsorption–desorption isotherms of WS_2/ZnS and (b) pore-size distribution of WS_2/ZnS.

B, which had already been absorbed by WS_2. The catalyst reuse experiment proved our point. As shown in Fig. 3b, repeated photocatalytic experiments prove that ZnS has low catalytic performance but good recyclability. However, WS_2 had poor repeatability in the repeatability experiment, indicating that adsorption performance was dominant in the treatment of pollutants of WS_2. In contrast, the WS_2/ZnS composite prepared by us had high repeatability. After the WS_2/ZnS catalyst was recovered and used 5 times, the catalytic activity was still close to that of the first use. In addition, the ability of the WS_2/ZnS composite to treat complex organic pollutants in water environment (containing three different dyes, rhodamine B, methylene blue and crystal violet) was also tested. As shown in Fig. 3c, the WS_2/ZnS composite also has good absorption-catalytic activity for complex polluted water environments, and can still treat more than 90% of pollutants within 20 min. The results show that the WS_2/ZnS composite material designed by us had high performance of adsorption-photocatalytic treatment of organic matter in water and efficient recovery and reuse performance.

3.4. Characterization of optical properties

From the above photocatalytic experiment, the ZnS material played a catalytic role in the composite materials,

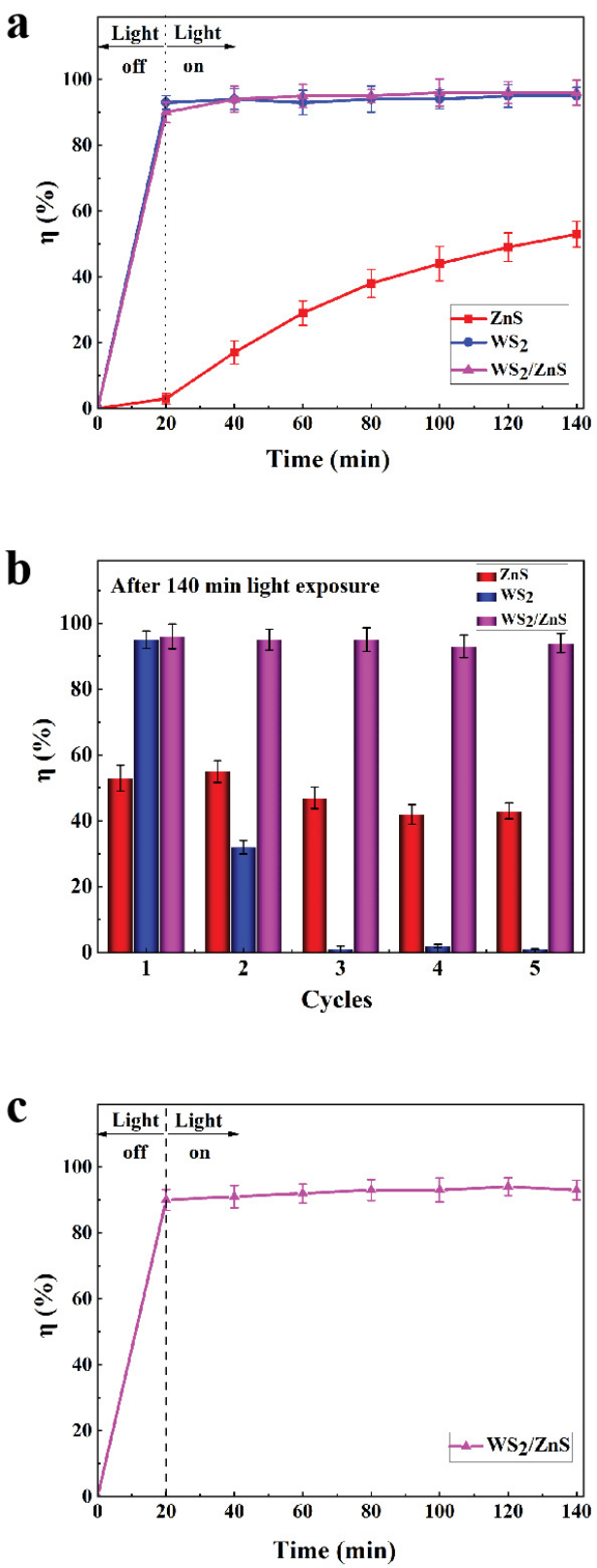

Fig. 3. (a) Photocatalysis efficiency (η) of rhodamine B by ZnS, WS_2 and WS_2/ZnS, (b) photocatalytic properties of the three materials for recycling and (c) photocatalysis efficiency (η) of the dye mixture by WS_2/ZnS.

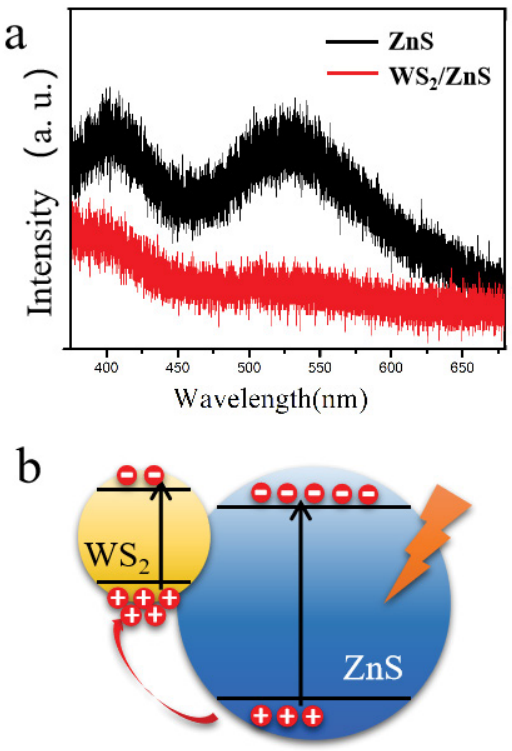

Fig. 4. (a) Photoluminescence spectra of WS_2/ZnS and ZnS and (b) energy band and electron transfer diagram of WS_2 and ZnS.

while WS_2 mainly played a role in absorbing pollutants. To analyze whether WS_2 played other roles, we tested the photoluminescence spectra of WS_2/ZnS and ZnS. It can be clearly seen from Fig. 4a that the ZnS material had strong luminescence peaks at 403 and 524 nm, which were mainly attributed to the radiation recombination of non-equilibrium carriers caused by the sulfur vacancy and zinc vacancy defect as the recombination center [26]. However, after ZnS was compounded by WS_2, the intensity of the two luminescence peaks decreased significantly. This is because the special band position of WS_2 leads the transfer of photogenerated carriers. As shown in Fig. 4b, the semiconductor heterojunction was formed after WS_2 contacts with ZnS. According to the minimum energy principle, the photogenerated holes generated by ZnS would be transferred to the valence band of WS_2 with lower energy. The transfer of carriers could effectively achieve the separation of electron holes, thus improving the life of photocarriers, and finally achieving the improvement of photocatalytic efficiency.

4. Conclusions

We have presented a novel WS_2/ZnS adsorption-catalyst, which has a good crystallization quality, a coarse surface morphology, and a high specific surface area (40.6 m^2/g). The WS_2/ZnS composite material combines the advantages of WS_2's high adsorption performance and ZnS's photocatalytic performance to quickly adsorb organic matter to its surface and then completely degrade the organic pollutants in water. WS_2/ZnS could effectively adsorb and catalyze 96% rhodamine B (100 mL of 10 mg/L) within 20 min. The WS_2/ZnS composite material could be reused, with performance remaining 98% of the first use after 5 uses. In addition, WS_2/ZnS also had excellent treatment ability for complex organic pollutants in water environment which was simulated by dyes. In summary, our results indicate that the WS_2/ZnS composite material has great potential for adsorption and photocatalytic performance, which will have great potential in the emergency treatment of organic matter in water.

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Conflicts of interest

The authors declare no competing financial interest.

Data availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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