

# Ag<sub>2</sub>S/WO<sub>3</sub> Composites with Full Spectrum Photocatalytic Activity

Biao Zhang<sup>a\*</sup>, HaiMing Zhang<sup>b</sup>, LiJuan Wei<sup>c</sup>

<sup>a,b</sup>*School of Science, Tianjin Polytechnic University, Tianjin 300387, People's Republic of China*

<sup>a</sup>*Email: 1061835565@qq.com*

<sup>b</sup>*Email: zhmtjwl@163.com*

## Abstract

The Ag<sub>2</sub>S/WO<sub>3</sub> composites were successfully prepared by two-step method. The composition, morphology and optical properties of the materials were characterized by XRD, EDS and SEM. The results show that the degradation rate of methylene blue (MB) in Ag<sub>2</sub>S/WO<sub>3</sub> composites is about 1.2 times higher than that in WO<sub>3</sub> under photocatalytic degradation under the same conditions. The reason is that this study has potential application value in the fields of solar cells and photochemical reactions due to the use of full spectrum to enhance photocatalytic efficiency.

**Keywords:** Ag<sub>2</sub>S/WO<sub>3</sub>; Z-band; full spectrum.

## 1. Introduction

WO<sub>3</sub> is an indirect bandgap semiconductor (E<sub>g</sub> = 2.4-2.8 eV) that absorbs about 12% of sunlight and absorbs visible light with a wavelength of nearly 500 nm. WO<sub>3</sub>'s wide band gap and narrow forbidden band width make it have good photoelectric response performance under visible light conditions, and it is superior to TiO<sub>2</sub> photo-response range and can be used for photocatalytic photoelectrochemical materials [1,2]. The photocatalytic efficiency of the WO<sub>3</sub> powder is not high because the photoexcited electron holes are easily recombined [3]. Therefore, finding a suitable method to suppress photogenerated electrons and hole recombination is an effective method to solve the low photocatalytic efficiency.

---

\* Corresponding author.

Ag<sub>2</sub>S is an n-type narrow bandgap semiconductor material with a forbidden band width of about 0.9-1.67 eV. It can absorb more visible light, can be excited by visible and infrared light, and has good photoelectric properties and high chemical stability [4]. However, experiments have shown that Ag<sub>2</sub>S powder has substantially no photocatalytic performance, because the photopolymerization electrons and holes have a high recombination rate, and the second is that Ag<sub>2</sub>S is easy to agglomerate, which also causes its photocatalytic activity to decrease. Therefore, selecting a suitable carrier to improve the dispersibility of Ag<sub>2</sub>S while suppressing photogenerated electrons and hole recombination is an effective method to solve the low photocatalytic efficiency. The Z-type photoreaction system is an important part of the photosynthesis photoreaction phase and consists of two photochemical reactions and an intermediate enzymatic redox reaction [5,6]. The electron transfer process forms a shape similar to the English letter "Z" and is therefore referred to as the Z-type reaction system [7,8]. This system was first proposed by Bard in 1979 after studying the photosynthesis of plants. The quantum efficiency of the reaction is close to 100% and the system has three major advantages: one is the two-photon excitation process, and the oxidation reaction and the reduction reaction are respectively performed on different photocatalysts. Second, the two-step photocatalyst only needs to satisfy the respective photoexcitation processes, which reduces the thermodynamic requirements of the photocatalytic reaction. Third, the oxidation reaction and the reduction reaction are separated from each other, and the occurrence of the reverse reaction is effectively suppressed. Based on the above situation, the Z-type band structure supported by WO<sub>3</sub> as the carrier and Ag<sub>2</sub>S is designed. In theory, it can not only inhibit the electron hole recombination of WO<sub>3</sub> and Ag<sub>2</sub>S, but also broaden the light absorption range of the photocatalyst to achieve ultraviolet, visible, and Infrared full-spectrum photocatalysis to enhance photocatalytic efficiency.

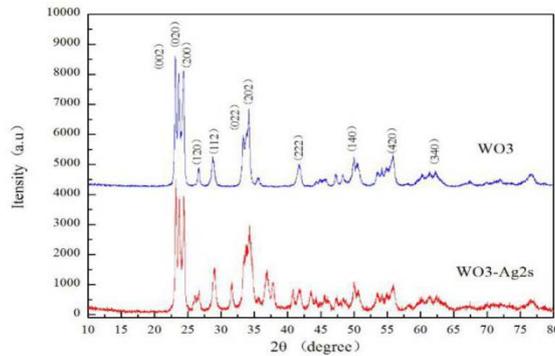
## 2. Experiments

4 g of ammonium metatungstate (AMT) was weighed, added to 20 ml of deionized water, and magnetically stirred at room temperature for 24 hours to form a uniform transparent solution. Dry in a constant temperature oven at 60 °C for 12 h under dark conditions. The mixture was placed in a tube furnace at a rate of 10 °C per minute to 500 °C, maintained at a constant temperature for 3 hours, and then cooled to room temperature at a rate of 10 °C per minute, and taken out to obtain a yellow WO<sub>3</sub> powder. Secondly, accurately weigh 0.5 g of WO<sub>3</sub> dissolved in 100 ml of deionized water, add 0.7326 g of AgNO<sub>3</sub>, magnetically stir for two hours, and record it as solution A; accurately weigh 0.5179 g of Na<sub>2</sub>S·9H<sub>2</sub>O dissolved in 100 ml of deionized water, magnetically stir two hours, recorded as B solution; pour B solution into the magnetic stirring A solution, continue to stir with a magnetic stirrer for one and a half hours, let stand for 40 min, wash with deionized water and absolute ethanol eight times, in the dark conditions The oven was dried at 60 °C for 12 h. Weigh 0.2 g MB and dissolve it in 1 L of water. After magnetic stirring, take 250 ml of MB solution into a 500 ml glass, and add 0.1 g of WO<sub>3</sub>/Ag<sub>2</sub>S to it and place it in a dark room photoreactor. The mixed reaction solution was magnetically stirred for 30 min in a dark room reactor in a dark room reactor to achieve adsorption-desorption equilibrium. 5 ml of the sample supernatant was taken, and then a 300 W xenon lamp was placed at a distance of about 12 cm from the reactor. Under the irradiation, magnetic stirring was carried out while photocatalytic degradation was carried out. 5 ml of the sample supernatant was taken every 15 min, and the absorbance A was measured at the maximum absorption wavelength of MB (664 nm). According to Lambert Beer's law, the degradation rate of dyes is  $E = (1 - A/A_0) \times 100\% = (1 - C/C_0) \times 100\%$  where A is the absorbance of MB during the

reaction; A0 is the initial of MB. Absorbance; C is the mass concentration of MB during the reaction; C0 is the initial concentration of MB.

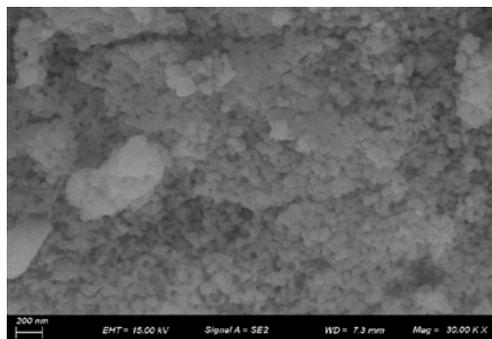
### 3. Results and discussion

Figure 1 is Comparison of XRD patterns of WO<sub>3</sub>/Ag<sub>2</sub>S and WO<sub>3</sub>. It can be seen that diffraction peaks, diffraction peaks of powder can be observed at diffraction angles close to  $2\theta = 23.119^\circ, 23.586^\circ, 24.380^\circ, 26.594^\circ, 28.937^\circ, 33.266^\circ, 34.155^\circ, 41.906^\circ, 49.948^\circ, 55.957^\circ$ . (002), (020), (200), (112), (120), (022), (202), (222), (140) of WO<sub>3</sub> (JCPDS card #43-1035) with monoclinic phase. The (420) crystal faces correspond one-to-one, which proves that the monoclinic crystal form WO<sub>3</sub> still exists, and the extra peaks are caused by Ag<sub>2</sub>S.  $2\theta$  increases the (111) peak of Ag<sub>2</sub>S between  $25^\circ$  and  $30^\circ$ , and increases the (112) peak of Ag<sub>2</sub>S between  $30^\circ$  and  $35^\circ$ , and increases the (121) of Ag<sub>2</sub>S between  $35^\circ$  and  $40^\circ$ . 103) Peaks, (031) and (022) peaks of Ag<sub>2</sub>S were added between  $40^\circ$  and  $45^\circ$ . All the extra peaks correspond to the peaks on the XRD pattern of Ag<sub>2</sub>S, demonstrating that monoclinic phase Ag<sub>2</sub>S still exists. In addition, after comparison, it was found that the XRD pattern of WO<sub>3</sub>/Ag<sub>2</sub>S was red-shifted compared to the XRD pattern of WO<sub>3</sub>.



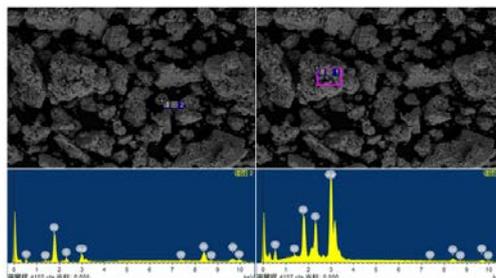
**Figure 1:** Comparison of XRD patterns of WO<sub>3</sub>/Ag<sub>2</sub>S and WO<sub>3</sub>

Figure 2 is SEM image of WO<sub>3</sub>/Ag<sub>2</sub>S. Under the 200 nm scale, it was found that Ag<sub>2</sub>S was spherically densely dispersed on WO<sub>3</sub>, and the design of loading Ag<sub>2</sub>S with WO<sub>3</sub> as load was realized. In addition, Ag<sub>2</sub>S is uniform in size and spherical, with a size of about 70 nm.



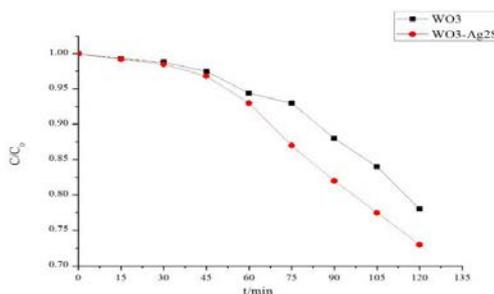
**Figure 2:** SEM image of WO<sub>3</sub>/Ag<sub>2</sub>S

Figure 3 is EDS of WO<sub>3</sub>/Ag<sub>2</sub>S. Whether it is a large particle or a small particle powder contains W element, O element, Ag element, S element, after normalization analysis and atomic percentage comparison, it is proved to contain WO<sub>3</sub> and Ag<sub>2</sub>S.



**Figure 3:** EDS of WO<sub>3</sub>/Ag<sub>2</sub>S

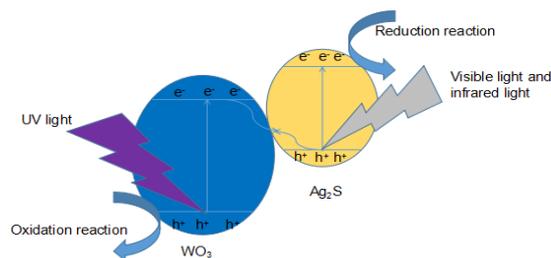
Figure 4 is Degradation curve of MB on WO<sub>3</sub> and WO<sub>3</sub>/Ag<sub>2</sub>S composites under ultraviolet-visible-infrared illumination. The photocatalytic effect of WO<sub>3</sub>/Ag<sub>2</sub>S on MB solution is better than that of WO<sub>3</sub> on MB solution. Under the condition of 120 min, the photocatalytic degradation effect of WO<sub>3</sub>/Ag<sub>2</sub>S was 1.2 times that of WO<sub>3</sub>.



**Figure 4:** Degradation curve of MB on WO<sub>3</sub> and WO<sub>3</sub>/Ag<sub>2</sub>S composites under ultraviolet-visible-infrared illumination

Figure 5 is Schematic diagram of WO<sub>3</sub>/Ag<sub>2</sub>S Z energy band structure. After UV3 absorbs ultraviolet light under ultraviolet light, the electrons in the valence band are excited through the forbidden band to transition from the valence band to the conduction band, while generating corresponding holes in the valence band, while being exposed to visible light and infrared light. The electrons in the Ag<sub>2</sub>S valence band are excited through the forbidden band to transition from the valence band to the conduction band, while generating corresponding holes in the valence band. Then the electrons on the conduction band of WO<sub>3</sub> and the holes on the valence band of Ag<sub>2</sub>S recombine, and the electrons on the conduction band of WO<sub>3</sub> and the holes on the WO<sub>3</sub> valence band are recombined, and the electrons on the conduction band of Ag<sub>2</sub>S and the valence band of Ag<sub>2</sub>S are suppressed. The holes recombine. As a result, holes are left on the valence band of WO<sub>3</sub> to react with -OH adsorbed on the surface of the catalyst particles to form ·OH, thereby oxidizing with organic contaminants, while leaving electrons on the conduction band of Ag<sub>2</sub>S. H<sub>2</sub>O and O<sub>2</sub> on the surface of the catalyst particles act to form O<sub>2</sub><sup>-</sup>, thereby reducing the reaction with organic pollutants. The photocatalytic process achieves inhibition of the respective electron hole recombination and full-spectrum photocatalysis using ultraviolet light,

visible light, and infrared light, thereby improving photocatalytic efficiency.



**Figure 5:** Schematic diagram of WO<sub>3</sub>/Ag<sub>2</sub>S Z energy band structure

#### 4. Conclusions

The Ag<sub>2</sub>S/WO<sub>3</sub> composites were successfully prepared. Under the same conditions, the degradation rate of methylene blue (MB) in Ag<sub>2</sub>S/WO<sub>3</sub> composites was higher than that of WO<sub>3</sub> materials under photocatalytic degradation conditions, which was about 1.2 times higher. This research has potential application value in the fields of solar cells and photochemical reactions.

#### Acknowledgements

This work is Supported by National Natural Science Foundation of China (61274064)

#### References

- [1]. Gar A M, Ookawara S, Fukushi D, et al. Improved WO<sub>3</sub> photocatalytic efficiency using ZrO<sub>2</sub> and Ru for the degradation of carbofuran and ampicillin.[J]. Journal of Hazardous Materials, 2016, 302:225-231.
- [2]. Nashed R, Alamgir F M, Soon Jang S, et al. Bandgap bowing in Ta-W-O system for efficient solar energy conversion: Insights from density functional theory and X-ray diffraction[J]. Applied Physics Letters, 2013, 103(13):6446.
- [3]. Dozzi M V, Marzorati S, Longhi M, et al. Photocatalytic activity of TiO<sub>2</sub>-WO<sub>3</sub> mixed oxides in relation to electron transfer efficiency[J]. Applied Catalysis B Environmental, 2016, 186:157-165.
- [4]. Kong E, Chang Y, Park H, et al. Quantum Dots: Bandgap Tuning by Using a Lattice Distortion Induced by Two Symmetries That Coexist in a Quantum Dot (Small 7/2014)[J]. Small, 2014, 10(7):1300-1307.
- [5]. Li P, Li H J, Tu W G, et al. Photocatalytic application of Z-type system[J]. Acta Physica Sinica, 2015, 64(9):448.
- [6]. Yanrui Li, Leilei Li, Yunqi Gong. Towards full-spectrum photocatalysis: Achieving a Z-scheme between Ag<sub>2</sub>S and TiO<sub>2</sub> by engineering energy band alignment with interfacial Ag[J]. 2015, 8(11):3621-3629.
- [7]. L W.Z 型 Ag<sub>3</sub>PO<sub>4</sub>/Ag<sub>2</sub>MoO<sub>4</sub> 异质结光催化剂构建和光催化降解有机污染物[J]. 催化学报, 2017, 38(2):337-347.
- [8]. Ho W. 二氧化钛基 Z 型光催化剂综述(英文)[J]. 催化学报, 2017, 38(12):1936-1955.