Ag$_2$S/WO$_3$ Composites with Full Spectrum Photocatalytic Activity

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Abstract

The Ag$_2$S/WO$_3$ 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$_2$S/WO$_3$ composites is about 1.2 times higher than that in WO$_3$ 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$_2$S/WO$_3$; Z-band; full spectrum.

1. Introduction

WO$_3$ is an indirect bandgap semiconductor ($E_g = 2.4-2.8$ eV) that absorbs about 12% of sunlight and absorbs visible light with a wavelength of nearly 500 nm. WO$_3$'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$_2$ photoresponse range and can be used for photocatalytic photoelectrochemical materials [1,2]. The photocatalytic efficiency of the WO$_3$ 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.
Ag2S 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 Ag2s powder has substantially no photocatalytic performance, because the photopolymerization electrons and holes have a high recombination rate, and the second is that Ag2S is easy to agglomerate, which also causes its photocatalytic activity to decrease. Therefore, selecting a suitable carrier to improve the dispersibility of Ag2S 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 WO3 as the carrier and Ag2S is designed. In theory, it can not only inhibit the electron hole recombination of WO3 and Ag2S, 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 WO3 powder. Secondly, accurately weigh 0.5 g of WO3 dissolved in 100 ml of deionized water, add 0.7326 g of AgNO3, magnetically stir for two hours, and record it as solution A; accurately weigh 0.5179 g of Na2S·9H2O 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 WO3/Ag2S 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 $E = (1 - A/A0) \times 100\% = (1 - C/C0) \times 100\%$ where A is the absorbance of MB during the
reaction; \( A_0 \) is the initial of MB. Absorbance; \( C \) is the mass concentration of MB during the reaction; \( C_0 \) is the initial concentration of MB.

3. Results and discussion

Figure 1 is Comparison of XRD patterns of WO\(_3\)/Ag\(_2\)S and WO\(_3\). 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\(_3\) (JCPDS card #43-1035) with monoclinic phase. The (420) crystal faces correspond one-to-one, which proves that the monoclinic crystal form WO\(_3\) still exists, and the extra peaks are caused by Ag\(_2\)S. \( 2\theta \) increases the (111) peak of Ag\(_2\)S between 25\(^\circ\) and 30\(^\circ\), and increases the (112) peak of Ag\(_2\)S between 30\(^\circ\) and 35\(^\circ\), and increases the (121) of Ag\(_2\)S between 35\(^\circ\) and 40\(^\circ\), (031) and (022) peaks of Ag\(_2\)S were added between 40\(^\circ\) and 45\(^\circ\). All the extra peaks correspond to the peaks on the XRD pattern of Ag\(_2\)S, demonstrating that monoclinic phase Ag\(_2\)S still exists. In addition, after comparison, it was found that the XRD pattern of WO\(_3\)/Ag\(_2\)S was red-shifted compared to the XRD pattern of WO\(_3\).

![Figure 1: Comparison of XRD patterns of WO\(_3\)/Ag\(_2\)S and WO\(_3\)](image)

Figure 2 is SEM image of WO\(_3\)/Ag\(_2\)S. Under the 200 nm scale, it was found that Ag\(_2\)S was spherically densely dispersed on WO\(_3\), and the design of loading Ag\(_2\)S with WO\(_3\) as load was realized. In addition, Ag\(_2\)S is uniform in size and spherical, with a size of about 70 nm.

![Figure 2: SEM image of WO\(_3\)/Ag\(_2\)S](image)
Figure 3 is EDS of WO3/Ag2S. 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 WO3 and Ag2S.

Figure 3: EDS of WO3/Ag2S

Figure 4 is Degradation curve of MB on WO3 and WO3/Ag2S composites under ultraviolet-visible-infrared illumination. The photocatalytic effect of WO3/Ag2S on MB solution is better than that of WO3 on MB solution. Under the condition of 120 min, the photocatalytic degradation effect of WO3/Ag2S was 1.2 times that of WO3.

Figure 4: Degradation curve of MB on WO3 and WO3/Ag2S composites under ultraviolet-visible-infrared illumination

Figure 5 is Schematic diagram of WO3/Ag2S 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 Ag2S 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 WO3 and the holes on the valence band of Ag2S recombine, and the electrons on the conduction band of WO3 and the holes on the WO3 valence band are recombined, and the electrons on the conduction band of Ag2S and the valence band of Ag2S are suppressed. The holes recombine. As a result, holes are left on the valence band of WO3 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 Ag2S. H2O and O2 on the surface of the catalyst particles act to form O2-, 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 WO3/Ag2S Z energy band structure

4. Conclusions

The Ag2S/WO3 composites were successfully prepared. Under the same conditions, the degradation rate of methylene blue (MB) in Ag2S/WO3 composites was higher than that of WO3 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

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References