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The photocatalytic performance of Ag$_2$S under visible and near-infrared light irradiation and its degradation mechanism

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Abstract:

Silver sulfide was rarely investigated as photocatalyst directly although it had been widely used as an important component of composite photocatalyst. In this study, Ag$_2$S, was synthesized by a facile ion-exchange method at room temperature and used directly as an effective photocatalyst. The results confirmed the excellent photo-oxidation performance of Ag$_2$S since methyl orange can be completely photo-degraded with Ag$_2$S in 30 min and 70 min under visible light and near-infrared light irradiation, respectively. This performance should ascribe to the narrow band gap of Ag$_2$S, 1.078 eV, and lower recombination efficiency of photogenerated electron-hole pairs of Ag$_2$S in photocatalytic process. The active specie employed in the photooxidation process with Ag$_2$S was identified as the anion ozone radicals. Such simple preparation and high photocatalytic performance of Ag$_2$S broadens its possible application for the future.

Keyword: Silver sulfide, photocatalyst, visible light, near-infrared light, methyl orange.
1. Introduction

As well known, the frequently-used photocatalyst, TiO$_2$, usually worked under ultraviolet light with high stability and low cost$^{1-3}$, but its low utilization of solar light restricted its future application. Therefore, the photocatalysts worked under wider solar spectrum such as visible light which occupied about 48% of the solar spectrum, even infrared light which occupied about 44% of the solar light$^4$ are focused and explored significantly for higher solar light utilization. In order to achieve high efficiency photocatalysts under wider solar spectrum irradiation, varied methods, such as nonmetals$^5$ or metals$^6$ doped TiO$_2$ photocatalysts, composite semiconductor photocatalysts$^7$, and new photocatalysts with small band gap$^8$ are attempted. Currently, some photocatalysts, which can work under visible and near-infrared light irradiation, such as YF$_3$:Yb$^{3+}$,Tm$^{3+}$/TiO$_2$$^9$, Cu$_2$(OH)PO$_4$$^{10}$, Bi$_2$WO$_6$/TiO$_2$$^{11}$, CQDs/Cu$_2$O$^{12}$, BiVO$_4$/CaF$_2$:Er$^{3+}$,Tm$^{3+}$,Yb$^{3+}$ and NaYF$_4$:Yb,Tm/ CdS/TiO$_2$$^{14}$, were reported and focused. However, the preparation program of most of them was complicated for mass production, and the consumed time for photo-degradation of organics under NIR irradiation was as long as two hours, four hours or even fifty hours. So it was necessary to develop an efficient photocatalytic material with simple preparation and higher activity in both cases of under visible light and NIR light.

Silver sulfide, Ag$_2$S, was an important chalcogenide compound and had been investigated for numerous applications such as photoconductors, photovoltaic cells, and superionic conductors, due to its good chemical stability and excellent optical limiting properties$^{15}$. In the field of photocatalysis, Ag$_2$S was mainly combined with other semiconductor catalysts to form a composite photocatalyst, improving the performance of bulk photocatalyst. Yi Xie, et al.$^{16}$ reported that after coupling with Ag$_2$S, TiO$_2$
nanocomposites could have a visible-light absorption capability; B. Subash, et al.\textsuperscript{17} proved that the photocatalytic efficiency of ZnO was enhanced by loading Ag\textsubscript{2}S; Shen et al.\textsuperscript{18} confirmed that the CdS nanostructures with highly dispersed Ag\textsubscript{2}S had the highest photocatalytic activity for hydrogen evolution when the concentration of Ag\textsubscript{2}S was 5\% by weight. Other composite photocatalysts contained Ag\textsubscript{2}S such as Ag\textsubscript{2}S/ZnIn\textsubscript{2}S\textsubscript{4}\textsuperscript{19}, ZnS-In\textsubscript{2}S\textsubscript{3}-Ag\textsubscript{2}S\textsuperscript{20}, Ag\textsubscript{2}S/MCM-41\textsuperscript{21} and Ag\textsubscript{2}S-coupled ZnO/ZnS\textsuperscript{22}, all exhibit good photocatalytic activity.

These successful examples of photocatalytic performance intensification with Ag\textsubscript{2}S implied that Ag\textsubscript{2}S should have the potential to be an effective photocatalyst. However, only a few investigations on the photocatalytic performance of pure Ag\textsubscript{2}S as photocatalyst were reported only as the comparison with the other photocatalysts without systematic study. Wenlong Yang et al.\textsuperscript{23} mentioned that only 7.8\% of the MO was degraded by the pure Ag\textsubscript{2}S sample after 30 min under visible-light irradiation; A. Pourahmad et al.\textsuperscript{21} pointed out that 41\% degradation of methylene blue by pure Ag\textsubscript{2}S within 60 min under UV light; D. Amaranatha Reddy, etc.\textsuperscript{24} photodegraded Rhodamine B with Ag\textsubscript{2}S, and the conversion was 21.78\% after 120 min under sunlight irradiation.

The existed results may suggest that the photocatalytic performance of pure Ag\textsubscript{2}S was unsatisfactory. But the low band gap energy (0.9 - 1.05 eV)\textsuperscript{25} of Ag\textsubscript{2}S with conductive band (CB) level of about 0 eV vs. NHE\textsuperscript{26} meant that it had absorption in the ultraviolet, visible and near-infrared regions, which made Ag\textsubscript{2}S an possible semiconductor material for photocatalytic application under visible and NIR light. Thus, it was worthy to systematically investigate the photocatalytic ability of pure Ag\textsubscript{2}S for its potential application for degradation of organic persistent pollutant.
In this research, pure Ag$_2$S photocatalyst was prepared by a facile ion-exchange method and employed to decompose MO under visible and NIR light irradiation. The morphology and structure of as-prepared Ag$_2$S were characterized, and its photocatalytic performance was investigated in detail. The working mechanism of Ag$_2$S was elucidated by means of simulation, electron spin resonance (ESR) analysis, and photodegradation experiments.

2. Experimental

2.1 Chemicals

All the reagents used in this work, including AgNO$_3$, Na$_2$S·9H$_2$O, methanol, indigo carmine and methyl orange (MO) were of analytic grade from the Chengdu Ke Long Chemical of China and were used directly without further treatment.

2.2 Preparation of the Ag$_2$S photocatalyst

The Ag$_2$S photocatalyst was prepared by a facile ion-exchange method at room temperature. In a typical process, 30 mL of Na$_2$S·9H$_2$O (0.1M) was dropped into the 40ML of AgNO$_3$ (0.2 M) solution by automatic titrator with dropping speed of 3.2 mL/min. After 30 min magnetic stirring, the black products were filtered and washed with deionized water more than 5 times to remove the unreacted components and the produced NaNO$_3$. Finally, the black powders were vacuum-dried at 60°C overnight in darkness. All the operations above were away from light as far as possible.

2.3 Characterizations

X-ray diffraction (XRD) patterns for Ag$_2$S powder samples were obtained by glancing angle X-ray diffraction (GA-XRD, X’Pert proMPD, the Netherlands) with a Cu Kα 40 kV/40 mA X-ray source (wavelength $\lambda$=0.15406 nm). The scanning electron
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microscopy (SEM) images and Energy Dispersive Spectrometer (EDS) analysis were taken with a JSM-7500F field emission scanning electron microscopy (JEOL). The transmission electron microscope (TEM) and high resolution transmission electron microscopic (HRTEM) images were taken with a Tecnai, G2, F20, S-TWIN microscope. X-ray photoelectron spectroscopy (XPS) measurements were performed on a VG ESCALAB MKII XPS system with Al Kα source and a charge neutralizer. The UV-Vis diffusion reflection spectra (UV-Vis DRS) of Ag$_2$S was acquired by using a UV-Vis spectrophotometer (TU-1901, Ge Beijing spectrometer, China) and fine BaSO$_4$ powder was used as a standard. Photoluminescence (PL) spectra were recorded with a fluorescence spectrometer (F-7000, Hitachi, Japan). The absorption spectrum of MO solution was obtained by using a UV-Vis spectrophotometer (TU-1901, Ge Beijing spectrometer, China). The particle size distribution of prepared Ag$_2$S samples was determined with a JL-1198 laser particle size analyser (Chengdu Jingxin powder analyser instruments Co., Ltd. China). The surface area of the photo-catalysts was determined by nitrogen adsorption method at –196°C with a BET analyzer (SSA-3500, China). FT-IR spectra of samples were recorded with KBr pellet in the range of 4000–400 cm$^{-1}$ on a FT-IR spectrometer (Spectrum II L1600300, Perkin Elmer) at room temperature. The active species were investigated with an electron spin resonance analyzer of ER200-SRC.

2.4 Measurement of photocatalytic activity

The photocatalytic activities of the samples were evaluated by the degradation of MO under visible and NIR light irradiation in an OCRS-IV photoreactor system, which included a 500 W Xe lamp and a 500 W mercury lamp, a cut-off filter with specified light wavelength and a water filter. About 0.1g of Ag$_2$S photocatalysts were placed in a
quartz tube of reactor with 10 mL aqueous MO solution (16mg/L). The suspensions were stirred for 120 min in darkness to reach the adsorption–desorption equilibrium. After that, the visible light (wavelength>380nm) or NIR light (wavelength>850nm) irradiation were switched on to start the photodegradation reaction. After the schedule time, the photoreaction was terminated, and the suspension was sampled and centrifuged to remove the solid particles. Then the concentration of MO solution was determined by using a UV–Vis spectrophotometer. The corresponding standard absorption curve of MO solution was shown in Fig. S3.

2.5 The theoretical calculations

The theoretical calculations were performed using the plane-wave pseudopotential DFT method. The ion-electron interaction was modeled by ultrasoft pseudopotential in the Vanderbilt form. The energy cutoff for a plane wave basis set was 400eV, and a Monkhorst-Pack k-mesh of $6 \times 6 \times 6$ was used. Geometry optimizations were done before single-point energy calculation, and self-consistent convergence accuracy was set at $1 \times 10^{-6}$ eV/atom. The convergence criterion for the maximal force between atoms was 0.01eV. The maximum displacement was $5 \times 10^{-4}$ Å, and the stress was 60 GPa. The $U_p$ parameter for S was 7 eV, and the $U_d$ parameter for Ag was 13.2 eV. Due to complete symmetry between spin-up and spin-down states, we only showed the spin-up results in this paper.

In general, the $U_d + U_p$ increases the splitting between occupied and empty energy levels since the correction is dependent on the occupancy of the orbitals. The energy band structure employing GGA+U, where $U_{S,p} = 7$ eV, $U_{Ag,d} = 13.2$ eV was taken.
3. Results and discussion

3.1 Characterization of the photocatalyst

The appearance of the as-prepared Ag$_2$S sample was black or dark brown powders. Its surface morphology, structure, and band structure were characterized with XRD, XPS, SEM, EDS and UV-Vis DRS.

3.1.1 XRD analysis

Crystallization and phase identification of Ag$_2$S with XRD were shown in Fig.1-a. The diffraction peaks of the curve were assigned to monoclinic Ag$_2$S (JCPDS No. 65-2356) with the lattice constants $a = 4.230$ Å, $b = 6.910$ Å, and $c = 7.870$ Å. No obvious impurity peaks was observed. According to the data of XRD, the crystallite size of Ag$_2$S was determined to be 32.6 nm by using the Debye-Scherrer equation:

$$D = \frac{k\lambda}{\beta \cos \theta}$$

where $D$ was the crystallite size of the catalyst, $K$ was dimensionless constant, $\lambda$ was the wavelength of X-ray(0.15406 nm), $\beta$ was the full width at half-maximum of the diffraction peak and $\theta$ was the diffraction angle.

3.1.2 XPS analysis.

X-ray photoelectron spectroscopy (XPS) measurements were performed to determine the possible existence of impurity elements such as N and Na, and the valence state of Ag atoms. Results in Fig. 1-b confirmed that no hetero atom such as N and Na was introduced in crystal, despite the fact that the catalyst was obtained from the reaction of the AgNO$_3$ and Na$_2$S in aqueous solution. This conclusion was in agreement to the EDS analysis results in Support Information Fig. S1

Peaks at 368.21 and 374.26 eV in Fig. 1-c should be assigned to Ag$_{3d5/2}$ and Ag$_{3d3/2}$ of Ag$^+$ ions in the Ag$_2$S photocatalyst$^{27}$. Meanwhile, peaks at 161.3 and 162.5 eV of the
S_{2p} photoelectron spectrum in Fig. 1-d were in perfect agreement with the binding energy of S_{2p3/2} and S_{2p1/2} of S^{2-}. It can be concluded that the as-prepared sample was constituted with pure Ag$_2$S without Ag and S atoms with other valences.

### 3.1.3 The microscopic surface structure and morphology of Ag$_2$S

As we all know, the crystalline structure of photocatalyst affected its photocatalytic activity. Therefore, the typical microscopic surface structure and morphology of the as-prepared Ag$_2$S were investigated by SEM and TEM.

Fig. 2-a was a typical SEM image of Ag$_2$S samples, which showed that Ag$_2$S particles were the aggregation of crystal grains with diameter of 30-80 nm, which was roughly consistent with the XRD results.

The result of TEM in Fig. 2-b confirmed that the size of Ag$_2$S aggregation was about 0.2 µm ~ 0.7 µm, which was consistent with the results obtained from laser particle size analyser (see Support Information Fig. S2) and BET analysis, the average particle size of 0.7226µm and the specific surface area of 6.062 m$^2$/g.

Fig. 2-c displayed the HRTEM image of Ag$_2$S sample, in which lattice fringes can be clearly observed. The clear fringes with an interval of 0.34 nm and 0.38 nm can be indexed to the (012) and (002) lattice plane of Ag$_2$S.

### 3.1.4 UV-Vis DRS analysis.

The UV-vis absorption spectra of the Ag$_2$S sample was shown in Fig. 3-a. The result revealed that the as-prepared Ag$_2$S sample had great absorption in the ultraviolet and visible regions, from which it could be inferred that Ag$_2$S should have great photocatalytic activity under ultraviolet light and visible light irradiation. Since the absorption edge of as-prepared Ag$_2$S samples was larger than 800 nm, which had
entered the spectrum of NIR light, it suggested the possibility of Ag$_2$S with photocatalytic activity in NIR region.

**Fig. 3-b** showed the results of UV-vis diffuse-reflectance spectroscopy, which usually was used to estimate the band gap of semiconductors. By plotting the $(ahv)^2 - hv$ (where $a$ is absorption coefficient and $hv$ is the photon energy) relationship$^{29}$, the band gap of as-prepared Ag$_2$S samples was estimated to be 1.078 eV, which was in agreement with the reported values$^{30}$.

### 3.1.5 PL analysis

It is well known that the photoluminescence (PL) signals of semiconductor materials resulted from the recombination of photoinduced charge carriers. In general, the lower the PL intensity, the lower the recombination rate of photoinduced electron–hole pairs, and the higher the photocatalytic activity of semiconductor photocatalysts$^{31,32}$. For this reason, the photoluminescence (PL) technique was used to identify the photocatalytic activity of Ag$_2$S.

In this study, the PL emission spectra of pure Ag$_2$S and pure TiO$_2$ were examined in the wavelength range of 300–700nm, and shown in **Fig. 4**. It was noted that an intensive PL spectrum of the pure TiO$_2$ is much higher than that in the spectra of Ag$_2$S samples. It can be reasonably inferred that the pure Ag$_2$S should have higher photocatalytic performance than TiO$_2$.

### 3.2 Photocatalytic activity

A typical persistent organic dye, methyl orange, was selected as the target compound of photodecomposition experiment for evaluating the photooxidation ability of Ag$_2$S. The adsorption and photodegradation of MO with Ag$_2$S as photocatalyst under visible and NIR light irradiation were determined.
3.2.1 Adsorption of MO on Ag$_2$S

The adsorption of MO on the surface of Ag$_2$S nanoparticles in dark was determined firstly to exclude its extra effect on the photocatalytic performance testing of photocatalyst. The result shown in Fig. 5 exhibited a sharp decrease of MO concentration from the starting time to zero. However, the adsorption-desorption equilibrium was still achieved after one hour, and after then, no significant decrease of MO concentration was observed.

3.2.2 Photo-degradation of MO with Ag$_2$S

After the achievement of adsorption equilibrium of MO with Ag$_2$S, the photocatalytic decomposition experiment of MO with Ag$_2$S under visible light and NIR light irradiation was conducted to evaluate the photocatalytic performance of Ag$_2$S. The MO degradation curve plotted in Fig. 5 displayed that the Ag$_2$S could completely degrade methyl orange in 30 min under visible light irradiation meanwhile in 70 min under near-infrared light irradiation. The repeatability experiments of MO degradation over Ag$_2$S was shown in Fig. S5.

The fast MO degradation rate with Ag$_2$S under NIR light irradiation should attribute to the huge surface area supplied by the aggregation structure of Ag$_2$S crystal grains, and strong absorption in visible and near-infrared light regions. However, the relatively slow decomposing rate of MO under NIR light irradiation comparing with under visible light irradiation should ascribe to the weak illumination of NIR light originating from the same Xe-lamp, which supplied the visible light illumination of 18-21 Klux, and NIR light illumination of 0.09-0.12Klux.
Such excellent property confirmed the assumption that Ag$_2$S can work under infrared spectrum with high degradation rate because of the narrow band gap, 1.078 eV, and high quantum efficiency. This outstanding photocatalytic activity and wide working spectrum of Ag$_2$S was attractive for further development.

3.2.3 FT-IR testing

It was necessary to determine the degradation of adsorbed MO on the surface of Ag$_2$S under light irradiation since about 40% MO had been adsorbed, regardless of the fact that MO in aqueous solution had been completely degraded under light irradiation. Two Ag$_2$S samples after reaching MO adsorption equilibrium were analyzed with FT-IR to determine the possible functional groups adhered on the surface of Ag$_2$S, and confirm the existence of the photodegradation of adsorbed MO. One was exposed in light for 30 minutes (1#), and the other was retained in darkness (2#).

The results shown in Fig. 6 confirmed the completely decomposition of adsorbed MO on the surface of Ag$_2$S. Peaks at 1601 cm$^{-1}$ and 814 cm$^{-1}$ of sample 2# should be assigned to the framework vibration of benzene ring and the two substituted phenyl, respectively. Such two characteristic peaks of MO were not observed at the corresponding position of FT-IR result of sample 1#.

Besides, sample 1# and 2# were soaked in deionized water respectively. The phenomenon (see in Support Information Fig. S4) and the result of FT-IR testing proved that MO can be completely photo-degraded with Ag$_2$S under light irradiation, no matter its existence was adsorbed or dissolved.

3.3. Photocatalytic mechanism of Ag$_2$S photocatalyst.

As well known, •OH radicals and photo-generated holes usually were possible active species in photocatalytic degradation process of organic pollutants. However, the large
electrode potential of •OH of 2.80 eV resulted in the possibility excluded in Ag$_2$S working mechanism since the band gap of Ag$_2$S was only 1.078 eV. It was necessary to find the possible active species and figure out the photocatalytic mechanism of Ag$_2$S under light illumination.

3.3.1 The determination of radical species

Spin trapping technique usually was employed to detect free radicals by “trap” a short-lived radical to generate a “long-lived” nitroxide radical, which can be monitored with conventional electron spin resonance methodology$^{33}$. Here the photocatalytic process of Ag$_2$S with and without light irradiation was investigated by ESR and the results were shown in Fig. 7. It could be observed that no significant ESR signal of Ag$_2$S was detected in darkness. On the contrary, a septet peak group with an intensity ratio of 1:2:2:2:2:2:1 was observed, which was consistent with the nitroxide DMPO-•O$_3$$^-$. This determined radical should be the ozone anion radicals$^{34}$. Since the unique signal of ozone anion radicals was the only one observed in solution with Ag$_2$S under light irradiation, it is safe to judge that such free radical was the proper photo-generated free radicals of Ag$_2$S in aqueous solution.

3.3.2 Radical-trapping experiments

Although the ozone anion radical was detected in light irradiation process of Ag$_2$S, it is necessary to determine the role of such radical played in photo-oxidation process. A radical-trapping experiment was conducted to identify the major active species in the degradation of MO on the surface of Ag$_2$S. Two scavengers, methanol and indigo carmine, were used to trap photo-generated hole and ozone. The possible masking effect disturbance of two scavengers in MO detection process with UV-Vis spectrophotometer was excluded based on the confirmatory results shown in Fig. 8-a. The MO degradation
results after adding varied scavengers were exhibited in Fig. 8-b. It can be observed that the addition of methanol decreased the MO photodegradation rate significantly since the photo-generated holes were trapped. However, addition of indigo carmine stopped the photo-oxidation process completely. This clear result confirmed that the combined function of photo-generated holes and ozone anion radicals under light irradiation dominated the reaction process of oxidative degradation of MO. The ozone anion radicals could be the major active specie in the photocatalytic process of Ag$_2$S.

3.3.3 DFT simulation of Ag$_2$S

For further understanding the electronic structure and chemical bonding mechanism of Ag$_2$S prepared, the *ab initio* density functional theory (DFT) calculations had been carried out. Fig. 9 was the crystal cell model used for DFT simulation of Ag$_2$S. The space group was based on P21/c (NO.14) that corresponds with the measured XRD results of as-prepared samples. Bond length of Ag$_2$S bond was provided as 2.692 Å, and bond angle was 105.894°.

The calculated band structure shown in Fig. 10 confirmed that Ag$_2$S was semiconductor with a direct band gap of 1.063 eV at the G point. This calculated value of Ag$_2$S band gap was slightly lower than the determined value, 1.078 eV, but more closer to the reported value, 1.05 eV$^{30}$. This slight discrepancy could be ascribed to the underestimation of the DFT, which considered only excited states in the calculation.

The calculated total density of states (TDOS) and partial density of states (PDOS) for Ag$_2$S was plotted in Fig. 11. The valence atomic configurations were 3s$^2$3p$^6$ for S and 4d$^{10}$ for Ag, respectively. The valence band of Ag$_2$S is clearly split into two regions. The lower region mostly likely has the S$_{3p}$ features whereas the upper one is dominated by Ag$_{4d}$ states. There were hybridized S$_{2p}$ states near the Fermi level, with little practical
contribution from Ag$_{5p}$ states that have a dominant weight in the bottom of the conduction band. For Ag$_2$S, the width of the valence band is equal to 10 eV. The S$_{3p}$ states have an intensity peak at 0.68 eV. In the upper region, the two Ag$_{4d}$ maxima are found at –9.2 eV and –7.18 eV.

3.3.5 Working mechanism of Ag$_2$S

In general, the photocatalytic activity of a photocatalyst is determined by the band gap and the oxidation potential of photo-generated holes. The conduction band (CB) and valence band (VB) potentials of Ag$_2$S at the point of zero charge was calculated by the equation\(^ {35}\) to investigate the oxidation potential of photo-generated holes:

\[
E_{VB} = X - E_e + 0.5E_g
\]

where \(X\) was the Pearson absolute electronegativity of the semiconductor, which was defined as the geometric mean of the absolute electronegativity of the constituent atoms\(^ {36}\), \(E_e\) was the energy of free electrons on the hydrogen scale (ca. 4.69 eV), \(E_{VB}\) is the VB edge potential, and \(E_g\) was the band gap of the semiconductor. The conduction band (CB) position can be determined by:

\[
E_{CB} = E_{VB} - E_g
\]

The \(X\) value for Ag$_2$S is ca. 4.968 eV\(^ {37}\). Based on the above equations, the top of the VB and the bottom of the CB of Ag$_2$S was calculated to be 0.992 eV and -0.072 eV, respectively. This result was concordant with that of the literature\(^ {38}\).

Based on the above analysis, the photo-oxidation mechanism of Ag$_2$S driven by light can be established and described as follows. Under light irradiation, Ag$_2$S was transformed into the excited state, generating excited electrons and holes on the surface or in the interior (1), simultaneously. The electrons and holes react with the oxygen (O$_2$) dissolved in aqueous solution and water molecules absorbed on the surface of Ag$_2$S
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particles, producing ozone anion radicals (2). Ozone anion radical, an extremely reactive specie, oxidize the organics (3). The photo-generated holes also can oxidize the organics directly (4).

The schematic diagram of the charge-transfer process in Ag$_2$S was shown in Fig. 12.

\[
\text{Ag}_2\text{S} + \text{hv} \rightarrow e^- + h^+ \quad (1)
\]

\[
\text{O}_2 + 2\text{OH}^- + 2h^+ + e^- \rightarrow \text{O}_3^- + \text{H}_2\text{O} \quad (2)
\]

\[
\text{O}_3^- + \text{dye} \rightarrow \text{oxidation products} \quad (3)
\]

\[
h^+ + \text{dye} \rightarrow \text{oxidation products} \quad (4)
\]
4. Conclusion

In summary, the Ag₂S photocatalyst has been successfully synthesized by a facile ion-exchange method. The as-prepared Ag₂S was the aggregation of crystal grains with diameter of 30-80 nm, and exhibited an excellent photocatalytic performance for the decomposition of MO under light irradiation. The complete degradation of MO with Ag₂S can be reached in 30 min under visible light illumination, and in 70 min under NIR light illumination, respectively. MO can be completely photo-degraded with Ag₂S under light irradiation, no matter its existence was adsorbed or dissolved. Such attractive performance should ascribe to the narrow band gap of Ag₂S, 1.078 eV, which was obtained by the theoretical calculations and the experiment. The PL spectrum of pure Ag₂S confirmed its high quantum efficiency. It was the combined function of photo-generated holes and ozone anion radicals of Ag₂S in aqueous solution under light irradiation dominated the reaction process of oxidative degradation of MO. The simple preparation method, excellent photocatalytic performance, and capability of working under NIR light irradiation of Ag₂S broadens its possible application for future as a promising photo-catalyst.
Acknowledgements

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Supporting Information Available

EDS and the particle size distribution of Ag$_2$S; The spectrum of methyl orange solution with different concentration; Extraction of adsorbed MO on Ag$_2$S with DI water; Repeatability experiments of MO degradation with Ag$_2$S under light irradiation.
References


Figure Caption

Figure 1. (a) XRD pattern of Ag$_2$S; (b) XPS survey spectra of Ag$_2$S; (c) Ag$_{3d}$ peaks of Ag$_2$S; and (d) S$_{2p}$ peaks of Ag$_2$S.

Figure 2. SEM, TEM and HRTEM analysis of Ag$_2$S: (a) SEM; (b) TEM; (c) HRTEM.

Figure 3. The UV-vis DRS spectra of Ag$_2$S.

Figure 4. The PL spectra of Ag$_2$S and TiO$_2$.

Figure 5. Photo-degradation of MO in aqueous solution: (a) with fresh Ag$_2$S under visible light; (b) with fresh Ag$_2$S under Near-infrared light.

Figure 6. FT-IR spectra of MO-adsorbed Ag$_2$S: after illumination (sample 1) and before light illumination (sample 2).

Figure 7. The ESR analysis of Ag$_2$S: under visible light illumination and in darkness.

Figure 8. Photodegradation of MO with Ag$_2$S: (a) The spectrophotometer spectra of different mixtures composed with pure MO, MO+ Methanol, MO+ indigo carmine, MO+ Methanol, pure MO. (b) The degradation curve of Ag$_2$S with MO + indigo carmine, MO + methanol, pure MO.
Figure 9. Unit-cell structure of Ag$_2$S. Yellow and blue spheres represent S, and Ag atoms, respectively.

Figure 10. Energy band structure and Density of State of Ag$_2$S.

Figure 11. TDOS and PDOS of Ag$_2$S.

Figure 12. The schematic diagram for the charge-transfer process in Ag$_2$S.
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