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Article

Enhanced photocatalytic performance of MoS₂ modified by AgVO₃ from improved generation of reactive oxygen species

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ABSTRACT

In this work, an efficient AgVO₃/MoS₂ composite photocatalyst was successfully synthesized via a hydrothermal method. The photocatalytic activity of the as-prepared photocatalyst was evaluated by using it for assessing the degradation of different organic pollutants under visible-light irradiation. The composite 3%-AgVO₃/MoS₂ catalyst demonstrated a significantly enhanced photocatalytic activity compared to the pure compounds (AgVO₃ and MoS₂). The reason behind the excellent photocatalytic performance was the modification of MoS₂ by AgVO₃ to facilitate O₂ adsorption/activation. In addition, the composite catalyst facilitates the two-electron oxygen reduction reaction whereby H₂O₂ is generated on the surface of MoS₂ to produce additional reactive oxygen species (ROSs). ESR coupled with the POPHA fluorescence detection method and a free radical capture experiment were used to elucidate the mechanism of formation of the ROSs, including •OH, •O₂⁻ and H₂O₂. Furthermore, the generation of additional ROSs could accelerate electron consumption, leaving behind more holes for the oxidation of organic pollutants. A possible photocatalytic mechanism of the composite is also discussed.

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1. Introduction

In recent years, the elimination of organic pollutants from the aquatic ecosystem has aroused much interest because of their association with certain environmental risks and their impact on the environment and human health [1–3]. Therefore, it is crucial to find an effective method to eliminate these organic pollutants. Visible light-driven semiconductor photocatalysts emerged as one of the most effective approaches toward solving energy and environmental pollution problems [4–7].

During photocatalytic degradation, molecular oxygen is activated by photogenerated electrons (e⁻) to generate the superoxide radical (•O₂⁻) and hydrogen peroxide (H₂O₂), while holes (h⁺) are trapped by surface-absorbed hydroxyl (OH⁻) to generate the hydroxyl radical (•OH), and •O₂⁻ react with h⁺ to produce singlet oxygen (¹O₂) [8]. These reactive oxygen species (ROSs) are regarded as the key oxidants for the CO oxidation, alcohol oxidation, and degradation of organic pollutants [9–11]. Many studies proved that the photocatalytic activity was dependent upon the absorption of visible light, separation of

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charge carriers, and surface chemical reactions [12]. However, the fabrication of a single semiconductor that possesses all of the above advantageous properties remained a great challenge.

Although the excitation of molybdenum disulfide (MoS_2) to generate charge carriers via visible light is well known, the redox potential of electron/hole in the conduction/valence band is not high, the quantum efficiency of molecular oxygen activation is suppressed, and the number of active sites on the surface of the photocatalyst is insufficient. Vast efforts had been focused on overcoming the above problems, including the construction of hybrid composite structures [13], metal doping [14], metal embedding [15], coupling with other semiconductors to form a heterojunction [16], and morphology control to expose a high-energy surface. However, the growing number of studies only focused on expanding the light absorption range and improving the separation efficiency of charge carriers. Reports on how to improve the activation efficiency of molecular oxygen were rare. It is worth noting that molecular oxygen plays a critical role in the production of ROSs [17]. Numerous semiconductor materials are known to be nonspecific in catalyzing ROSs production. Therefore, materials that specifically promote ROSs production needed to be combined with MoS_2 to further promote the photocatalytic activity. For example, He et al. [18] showed that the deposition of metal (Au) nanoclusters onto ZnO could greatly increase the generation of ROSs, resulting in the enhancement of photocatalytic activity, possibly because of the high oxygen active abilities of Au. Normally, the addition of metallic materials to a photocatalytic system improves the activation efficiency of the molecular oxygen. However, we would preferably choose metallic oxide to not only improve the separation efficiency of the photogenerated charge carriers, but also to increase the redox potential of electron/hole in the conduction/valence band, and hence enhance the photocatalytic activity.

Silver vanadium oxide (SVO) materials (AgVO_3 [19], $\text{Ag}_2\text{V}_4\text{O}_{11}$ [20], Ag_3VO_4 [21], and $\text{Ag}_4\text{V}_2\text{O}_7$ [22], etc.) attracted attention because of their widespread application in rechargeable high-energy-density lithium batteries [23], sensors [24], and photocatalysts [25,26]. However, AgVO_3 has a narrow band gap and highly dispersed valence band owing to the hybridized valence bands (V 3d, O 2p, and Ag 4d orbitals) [27], which means it shows potential application as a visible-light photocatalyst. These advantages of AgVO_3 motivated us to synthesize AgVO_3 -modified MoS_2 , which would promote the oxygen molecular reduction reaction and generate a larger number of ROSs to enhance the photocatalytic activity. Although work relating to $\text{AgVO}_3/\text{MoS}_2$ photocatalysts that could enhance the photocatalytic activity toward organic dyes degradation have been reported [28], the specific catalyzing features of AgVO_3 , in the $\text{AgVO}_3/\text{MoS}_2$ composites, in ROSs production were not discussed. We adopted an effective method using ESR coupled with a POPHA fluorescence detection method and free radical capture experiment to study the mechanism of the ROSs generated in the presence of photocatalyst. We found that AgVO_3 -modified MoS_2 could produce three kinds of ROSs, i.e., $\bullet\text{OH}$, $\bullet\text{O}_2^-$, and H_2O_2 . We concluded that the AgVO_3 in the $\text{AgVO}_3/\text{MoS}_2$ composites could act as a specific component to

catalyze ROSs production.

Herein, we report the ability of $\text{AgVO}_3/\text{MoS}_2$ to achieve an efficient photocatalytic degradation of pollutants. The charge transfer and molecular oxygen activation processes in the system were investigated to explore the possible reaction mechanism. Our work demonstrated a promising way to simultaneously increase the separation of charge carriers and the activation of molecular oxygen.

2. Experimental

2.1. Chemicals

All reagents were directly used as received without further purification. Silver nitrate (AgNO_3 , AR), p-benzoquinone (99.0%, AR), triethanolamine (TEOA, AR), and isopropanol (IPA, AR) were all purchased from Shanghai Chemical Reagent Co., Ltd., ammonium metavanadate (NH_4VO_3), sodium molybdate (Na_2MoO_4 , AR), thioacetamide ($\text{C}_2\text{H}_5\text{NS}$, AR), p-hydroxyphenylacetic acid (POPHA, AR), horseradish peroxidase (AR), tris(hydroxymethyl)aminomethane hydrochloride (Tris-HCl, AR), ethanol ($\text{C}_2\text{H}_5\text{OH}$, 95.0%), and ammonia solution ($\text{NH}_3\cdot\text{H}_2\text{O}$, 28%) were all supplied by Sinopharm Chemical Reagent Co., Ltd. TC, CIP, and RhB were analytically pure and used without further purification, and deionized water was used throughout these experiments.

2.2. Photocatalyst preparation

2.2.1. Synthesis of MoS_2

MoS_2 was prepared by using a hydrothermal method. In a typical procedure, 1.03 mmol Na_2MoO_4 was dispersed in 60 mL deionized water under stirring for 30 min. Subsequently, 2.66 mmol $\text{C}_2\text{H}_5\text{NS}$ was added to the above solution, which was stirred vigorously for 30 min. The solution was transferred to a Teflon-lined stainless-steel autoclave and maintained at 200 °C for 16 h. The sample was washed with deionized water and ethanol several times and then dried at 80 °C for 12 h.

2.2.2. Synthesis of $\text{AgVO}_3/\text{MoS}_2$ nanocomposite

The $\text{AgVO}_3/\text{MoS}_2$ nanocomposites were synthesized via a hydrothermal method. A certain amount of MoS_2 was added into 20 mL of AgNO_3 solution (3.6 mmol L^{-1}) under vigorous stirring. After 30 min, 20 mL of NH_4VO_3 solution (3.64 mmol L^{-1}) was appended to the above mixed solution in a drip. Then, the pH value of the solution was adjusted to approximately 7.0 with ammonia solution under stirring. This solution was subsequently transferred into a Teflon-lined stainless steel autoclave and maintained 180 °C for 24 h. Finally, the sample was washed with deionized water and ethanol several times, then dried in a vacuum oven at 80 °C for 12 h. The final products were named 1%- $\text{AgVO}_3/\text{MoS}_2$, 3%- $\text{AgVO}_3/\text{MoS}_2$, 5%- $\text{AgVO}_3/\text{MoS}_2$, and 7%- $\text{AgVO}_3/\text{MoS}_2$ according to the mass fraction of AgVO_3 in the MoS_2 by weight. The preparation process of $\text{AgVO}_3/\text{MoS}_2$ is shown in Scheme 1.

2.3. Characterization

Scheme 1. Schematic description of the synthesis procedures of $\text{AgVO}_3/\text{MoS}_2$ photocatalyst via the hydrothermal method.

Powder X-ray diffraction (XRD) measurements of the samples were performed with a D/max-RA X-ray diffractometer (Rigaku, Japan) using $\text{Cu-K}\alpha$ radiation in the scanning angle range of 10° – 80° at a scanning rate of 5° min^{-1} . Scanning electron microscopy (SEM) was conducted by using Hitachi S-4800 field emission SEM (Hitachi, Japan) to observe the morphology of the as-prepared samples. Transmission electron microscopy (TEM) was performed by using an F20 S-TWIN electron microscope (Tecnai G2, FEI Co.), equipped with a 200-kV accelerating voltage. The optical properties of the samples were carried out by UV-vis diffuse reflectance spectroscopy (DRS), recorded between 200 and 800 nm on a Shimadzu 2450 UV-vis spectrophotometer (Shimadzu, Japan) using BaSO_4 powder as a reference. The surface electronic states were investigated by X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250X) and an electron spectrometer using 150 W Al $K\alpha$ X-ray sources, and the binding energies were referred to the position of C 1s at 283.6 eV. The photoluminescence (PL) spectra of the solid photocatalysts were recorded on a F4500 (Hitachi, Japan) photoluminescence detector. The specific surface area and particle size of the materials were obtained via the Brunauer-Emmett-Teller (BET) method based on the N_2 adsorption-desorption isotherms (NDVA-2000e).

2.4. Photo-electrochemical measurements

Electrochemical impedance spectroscopy (EIS) was implemented in $0.5 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$ solution in the frequency range between 0.1 Hz and 10 kHz at 0.3 V. The amplitude of the applied sine wave potential in each case was 5 mV and was measured using a ZENNIUM electrochemical workstation (Zahner Instruments, Germany), and all electrochemical signals were recorded on a CHI660B electrochemical analyzer (Chen Hua Instruments, Shanghai, China).

2.5. Photocatalytic analysis

The photocatalytic activity of the $\text{AgVO}_3/\text{MoS}_2$ nanocomposites was evaluated by observing the degradation of TC, CIP, and RhB under visible light irradiation. Photocatalyst (0.05 g) was added to 100 mL of a pollutant solution (10 mg L^{-1}), and a 350-W Xenon lamp with a cutoff filter ($\lambda > 420 \text{ nm}$) was used as the light source. Light was excluded from the reaction system, which was magnetically stirred for 30 min to attain adsorption-desorption equilibrium before illumination. At certain time intervals, 4 mL aliquots were collected from the reaction process, centrifuged, and analyzed by UV-vis spectrophotometry.

2.6. Determination of ROSs during photocatalytic degradation

The ESR signals of radicals spin-trapped by 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO) were measured to detect the $\bullet\text{OH}$ and $\bullet\text{O}_2^-$ on a Bruker model ESR JES-FA200 spectrometer after irradiating the suspension with simulated sunlight (adding $20 \mu\text{L}$ DMPO) at different time intervals.

The production of H_2O_2 was determined by another fluorescence route by employing *p*-hydrophenylacetic acid (POPHA), which could be oxidized to the fluorescence product 5,5-dicarboxymethyl-2,2-dihydroxybiphenyl by a peroxidase-catalyzed reaction in the presence of H_2O_2 . Aliquots (0.5 mL) of irradiated catalyst solution were removed and maintained in the dark for 30 min. Subsequently, 0.5 mL of the fluorometric reagent (8 mg of POPHA and 2 mg of horseradish peroxidase dissolved in 50 mL of Tris buffer (0.1 mol L^{-1} , pH 8.8) solution) was added and allowed to react for 30 min. Then, the above solution was centrifuged, and the supernatant was recovered for fluorescence measurement.

3. Results and discussion

3.1. Characterization of the $\text{AgVO}_3/\text{MoS}_2$ composites

3.1.1. Structure and morphology characteristics

The XRD patterns of pure MoS_2 and $\text{AgVO}_3/\text{MoS}_2$ samples with different loading amounts of AgVO_3 are shown in Fig. 1. The pure MoS_2 sample displayed four broad XRD peaks at $2\theta = 14^\circ$, 33° , 43° , and 58° , corresponding to the (002), (100), (006), and (100) planes of hexagonal MoS_2 (JCPDS card No. 75-1539), respectively [29]. With AgVO_3 loaded on the surface of MoS_2 , the composites (1%, 3%, 5%, and 7%) showed diffraction peaks similar to those of pure MoS_2 , indicating that the introduction of AgVO_3 neither changed the phase of MoS_2 nor was it incorporated into the lattice of MoS_2 . Furthermore, an increase in the ratio of AgVO_3 to MoS_2 from 1% to 7% led to a remarkable reduction in the intensity of the MoS_2 diffraction peaks of the (002) and (110) planes, as well as the gradual disappearance of the diffraction peaks of the (002) plane, owing to the partial coverage of the surface of MoS_2 by AgVO_3 . The diffrac-

Fig. 1. XRD patterns of pure MoS_2 and $\text{AgVO}_3/\text{MoS}_2$ with various AgVO_3 loadings.

tion peaks assigned to AgVO_3 were not observed for the $\text{AgVO}_3/\text{MoS}_2$ composite materials, which might be due to the low content, i.e., the relatively weak diffraction intensity. However, the XPS, TEM, and SEM results adequately proved that AgVO_3 and MoS_2 were successfully combined.

The morphology and superficial microstructure of the as-prepared AgVO_3 , MoS_2 , and the composite material were characterized by TEM. Fig. 2(A) and (B) show the nanorod morphologies of pure AgVO_3 with smooth surfaces. Pure MoS_2 exhibited a nanoflower morphology (Fig. 2(C) and (D)), clearly showing that the MoS_2 nanoflowers consisted of several single layers of ultra-thin nanosheets overlapping each other, and the pure MoS_2 was an agglomerate. However, Fig. 2(E) shows that the MoS_2 was distributed on both sides of the AgVO_3 nanorods to prevent the agglomeration of MoS_2 . Fig. 2(F) clearly shows that the composite consisted of both MoS_2 and AgVO_3 , which are tightly combined with each other to form a compact hybrid structure. Two different inter-planar spacings (d) were observed to be 0.24 and 0.63 nm, which can be assigned to the (111) planes of AgVO_3 and (002) planes of MoS_2 . Therefore, the as-prepared photocatalyst had good dispersibility and was considered able to promote the exposure of reactive sites. The photocatalyst was therefore conducive to the transport of charge carriers on the interfaces of AgVO_3 and MoS_2 . The as-prepared samples were also investigated by SEM. Fig. S1(A) and (B) shows the SEM images of the AgVO_3 nanorods, which are approximately 100–500 nm wide and crossed together. The size of the MoS_2 nanoflowers was approximately 400–500 nm with their petals grown together in a disordered interweaved way and pointing towards the unity direction of the sphere to construct the spherical structure in Fig. S1(C) and (D). In the composite structure of $\text{AgVO}_3/\text{MoS}_2$, which was shown in Fig.

S1(E) and (F), the AgVO_3 nanorods and MoS_2 nanoflowers are linked together in accordance with the TEM results.

The surface chemical composition and chemical states of the 3%- $\text{AgVO}_3/\text{MoS}_2$ composite were analyzed by XPS, and the results are shown in Fig. 3. The full-scale XPS pattern of 3%- $\text{AgVO}_3/\text{MoS}_2$ is shown in Fig. 3(A), which indicates the existence of the elements C, Ag, V, O, Mo, and S. This result is consistent with the chemical composition of the as-prepared photocatalyst. The C 1s peak at approximately 283.6 eV could be assigned to the signal from carbon contained in the apparatus and was used for calibration [30]. Fig. 3(B) shows that the two strong peaks at approximately 368.01 and 374.02 eV could be attributed to $\text{Ag } 3d_{5/2}$ and $\text{Ag } 3d_{3/2}$, respectively. It confirmed that the Ag^+ existed in the photocatalyst [31,32]. As shown in Fig. 3(C), the V 2p peaks were observed at binding energies of 517 and 524.5 eV, which correspond to $\text{V } 2p_{5/2}$ and $\text{V } 2p_{3/2}$, respectively. The high-resolution O 1s spectrum shown in Fig. 3(D) indicates that the asymmetrical O 1s peak could be divided into two peaks located at 530.2 and 530.6 eV, which were ascribed to the oxygen ions in the fully oxidized surrounding and the oxygen ions in oxygen-deficient regions, respectively [33]. For pure MoS_2 (Fig. 3(E)), it was clearly observed that the peaks at 229.36 and 232.62 eV are those of the $\text{Mo } 3d_{5/2}$ and $\text{Mo } 3d_{3/2}$ of Mo^{4+} , respectively [34]. The peak at a binding energy of 226.49 eV was that of S 2s, consistent with the characteristic of S^{2-} . Obviously, apart from the XPS peaks of Mo^{4+} and S^{2-} , the peak for $\text{Mo } 3d$ at 233.09 eV was observed for the 3%- $\text{AgVO}_3/\text{MoS}_2$ composites, showing the existence of the Mo^{6+} state, which might be due to the formation of small amounts of surface oxide species during the hydrothermal reaction [35]. In addition, the $\text{Mo } 3d$ of Mo^{4+} in the 3%- $\text{AgVO}_3/\text{MoS}_2$ composite showed negative shifts in contrast to that of MoS_2 , suggesting that the chemical environment of Ag^+ had changed when AgVO_3 coupled with MoS_2 . For the S 2p spectra (Fig. 3(F)), the peak binding energies were centered at 162.25 and 163.55 eV for MoS_2 , and 161.08 and 162.55 for the 3%- $\text{AgVO}_3/\text{MoS}_2$ composites, respectively. Similarly, negative shifts were observed on the spectra of 3%- $\text{AgVO}_3/\text{MoS}_2$, indicating that the chemical environments of S^{2-} in the MoS_2 and the 3%- $\text{AgVO}_3/\text{MoS}_2$ composite were different. The negative shifts in the binding energy of $\text{Mo } 3d$ and S 2p in the 3%- $\text{AgVO}_3/\text{MoS}_2$ composites might be attributed to the existence of strong interaction between MoS_2 and AgVO_3 rather than simple physical adsorption. These results confirmed the successful formation of a heterojunction structure between AgVO_3 and MoS_2 .

3.1.2. Specific surface areas analysis

The specific surface areas and pore volumes of the prepared samples were further analyzed by nitrogen adsorption-desorption isotherm measurement. The image in the inset in Fig. 4 shows that all the samples had a mesoporous pore size (approximately 25–30 nm). Furthermore, according to the IUPAC classification, both isotherms belong to type IV physisorption isotherms. The characteristic features of this type of isotherm are its hysteresis loop associated with capillary condensation occurring in the mesoporous structure, and the limiting uptake in the range of high relative pressure [36,37]. The

Fig. 2. TEM images of AgVO_3 (A, B), MoS_2 (C, D), and 3%- $\text{AgVO}_3/\text{MoS}_2$ (E); HRTEM image of 3%- $\text{AgVO}_3/\text{MoS}_2$ (F).

Fig. 3. Full XPS patterns of 3%-AgVO₃/MoS₂ (A), Ag 3d (B), V 2p (C), O 1s (D), Mo 3d (E), and S 2p (F).

Fig. 4. N₂ adsorption-desorption curves and pore diameter distributions (inset) of MoS₂ (A) and 3%-AgVO₃/MoS₂ (B).

as-prepared photocatalysts displayed an H3-type hysteresis loop ($P/P_0 > 0.4$), which may have resulted from the MoS₂ nanoflowers consisting of several ultra-thin MoS₂ nanosheets overlapping each other. The BET surface area measurements of pure MoS₂ and 3%-AgVO₃/MoS₂ were 17.36 and 7.71 m² g⁻¹, respectively, demonstrating that the introduction of AgVO₃ influenced the surface area. The specific surface area and pore volume calculated from the isotherms are summarized in Table

1.

3.1.3. Optical properties

The UV-vis diffuse reflection spectra of the AgVO₃, MoS₂, and AgVO₃/MoS₂ composites with different loadings of AgVO₃ are also shown in Fig. 5. The pure MoS₂ showed significant absorption both in the ultraviolet and visible regions. For the pure AgVO₃, strong absorption at wavelengths shorter than ap-

Table 1 Specific surface areas and pore volumes of MoS₂ and 3%-AgVO₃/MoS₂.

Sample	S_{BET} (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)
MoS ₂	17.36	0.0647
3%-AgVO ₃ /MoS ₂	7.71	0.0788

Fig. 5. UV-vis diffuse reflection spectra of AgVO₃, MoS₂, and AgVO₃/MoS₂ with different AgVO₃ loadings.

proximately 500 nm was attributed to the intrinsic band gap absorption [38,39]. The optical absorption of the composite material increased after combining AgVO₃ with MoS₂ compared to that of pure MoS₂, suggesting that the composites possessed enhanced visible light photocatalytic properties. In addition, the band gap energy (E_g) of AgVO₃ and MoS₂ was calculated by:

$$(\alpha h\nu)^n = A(h\nu - E_g) \quad (1)$$

where α , h , ν , E_g , and A denote the absorption coefficient, Planck's constant, light frequency, band gap energy, and a constant, respectively. Among them, the index n depends on the type of optical transition of a semiconductor ($n = 1$ and 4 for direct and indirect transitions, respectively) [40,41]. For MoS₂, n was 2, and the corresponding Kubela-Munk transformed reflectance spectra are shown in Fig. S2. The band gap energy could be estimated from the intercept of the tangent to the plot of $(\alpha h\nu)^2$ vs. the radiation energy $(h\nu)^2$. The obtained band gap

energy for MoS₂ and AgVO₃ were 1.79 and 2.18 eV, respectively, which are consistent with the previous report [42,43].

3.2. Photocatalytic performance

3.2.1. Adsorption analysis

The adsorption capacity is one of the important properties of the photocatalytic degradation of pollutants. Fig. 6 displays the nonlinear fitting curves and linear fitting curves of pure AgVO₃, MoS₂, and 3%-AgVO₃/MoS₂ for adsorbing TC molecules, which could be used to study the adsorption performance with different as-prepared samples quantitatively. These adsorption experiments were carried out at room temperature and the adsorption kinetics could be described by the pseudo-second-order model [44]:

$$Q_t = \frac{kQ_e^2 t}{1 + kQ_e t} \quad (2)$$

where Q_e and Q_t (mg g⁻¹) are the amount of TC molecules adsorbed on samples at equilibrium and at time t , respectively, k (min⁻¹) is the equilibrium rate constant of pseudo-second-order adsorption (g mg⁻¹ min⁻¹). Here, a fast adsorption process with high rate constant is desired. The k values for these three processes with pure AgVO₃, MoS₂, and 3%-AgVO₃/MoS₂ were calculated by fitting the plots of t/q_t vs. t . The adsorption of TC obeyed the pseudo-second-order rate equation well because of the favorable agreement between experimental and calculated values of Q_e ($R^2 > 0.99$). The relevant data are provided in Table 2. The adsorption rate of MoS₂ was greatly improved when the AgVO₃ was combined with MoS₂. The enhanced adsorption capacity and improved adsorption rate constant might be regarded as one of the reasons for the enhanced photocatalytic degradation process.

3.2.2. Photocatalytic activity test

The photocatalytic degradation performance of as-prepared samples was evaluated under visible light irradiation ($\lambda > 420$ nm) using TC as the model organic contaminant. The degradation results in Fig. 7(A) show that the blank curve provides evidence of negligible degradation of TC, indicating that the TC

Fig. 6. Nonlinear fitting curves (A) and linear fitting curves (B) of pure AgVO₃, MoS₂, and 3%-AgVO₃/MoS₂ for adsorbing TC, where the lines represent the pseudo-second-order modeling results and fitting lines, respectively.

Table 2

Corresponding calculation results for adsorption test.

Sample	Q_e (mg g ⁻¹)	k (min ⁻¹)	R^2
MoS ₂	1.0031	0.8632	0.9997
AgVO ₃	1.3389	0.2874	0.9987
3%-AgVO ₃ /MoS ₂	3.2258	0.4189	0.9999

was stable under visible light irradiation. After visible light irradiation for 180 min, only 32.05% and 48.0% of pure MoS₂ and AgVO₃, respectively, were degraded. Furthermore, the composite photocatalytic activity first increased to a maximum and then decreased as the AgVO₃ loading on the surface of MoS₂ increased. The photocatalyst with optimal performance is 3%-AgVO₃/MoS₂, which indicated that the appropriate modification of MoS₂ with AgVO₃ played an important role in the improvement of the photocatalytic degradation efficiency. This tendency could possibly be attributed to the poor distribution of excessive AgVO₃ on the surface of MoS₂, which, together with agglomeration, leads to the weak transmitting ability of photo-generated electrons. The photo-degradation kinetic constants of different samples could be measured by the pseudo-first-order equation:

$$\ln(C_0/C) = kt \quad (3)$$

where k is the apparent kinetic rate constants, t is the irradiation time, and C and C_0 are the real-time concentration at t and the initial concentration of TC, respectively. As shown in Fig.

7(B), the apparent rate constant of 3%-AgVO₃/MoS₂ was 0.0087 min⁻¹, which is 1.71 and 1.76 times higher than those of MoS₂ (0.00509 min⁻¹) and AgVO₃ (0.00495 min⁻¹), respectively. To obtain improved insight into the catalytic performance of the 3%-AgVO₃/MoS₂ composites, RhB and CIP were also employed as target contaminants. As shown in Fig. 7(C), the results revealed that during the RhB and CIP photo-degradation process, the 3%-AgVO₃/MoS₂ also exhibited enhanced photocatalytic activity. The degradation efficiency of RhB and CIP was 83% and 62.4%, respectively, and the apparent rate constants of degradation of RhB and CIP were 0.0139 min⁻¹ and 0.00685 min⁻¹ (Fig. 7(D)), respectively. The improved photocatalytic performance owing to the modification of MoS₂ with AgVO₃ could facilitate O₂ adsorption/activation and thus generated a larger number of ROSs to degrade organic pollutants.

3.2.3. Stability performance

The stability and reusability of the photocatalyst were crucial factors to estimate the quality of photocatalyst and for subsequent practical application. To examine the stability of the 3%-AgVO₃/MoS₂, the photocatalyst was collected after degradation of TC for reuse. As shown in Fig. 8(A), the photocatalyst activity of 3%-AgVO₃/MoS₂ remained approximately 73% after four successive experimental cycles and showed almost no deactivation, revealing the improved stability of the photocatalyst during the process of degrading TC. The stability

Fig. 7. Photocatalyst degradation of TC (A) and the pseudo-first-order reaction kinetics for TC degradation (B) without a catalyst (a) and with MoS₂ (b), AgVO₃ (c), 1%-AgVO₃/MoS₂ (d), 3%-AgVO₃/MoS₂ (e), 5%-AgVO₃/MoS₂ (f), 7%-AgVO₃/MoS₂ (g); Photocatalytic degradation of CIP, TC, and RhB (C) and the pseudo-first-order reaction kinetics for CIP, TC, and RhB degradation (D) by as-prepared 3%-AgVO₃/MoS₂.

of the as-prepared photocatalyst was further investigated by recording the XRD patterns of the 3%-AgVO₃/MoS₂ before and after four cycles, as shown in Fig. 8(B). There is almost no difference between the two samples, with the main characteristic diffraction peaks of 3%-AgVO₃/MoS₂ being in almost the same position on the pattern, indicating that the crystal structure remained unchanged after the cycling tests. All the above results indicated that the 3%-AgVO₃/MoS₂ composite was an effective and stable photocatalyst for the degradation of contaminations. For the sake of investigating the stability of samples more thoroughly, the TEM images of the 3%-AgVO₃/MoS₂ before and after the cyclic experiment were acquired and are shown in Fig. 8(C) and (D). It can be observed from Fig. 8(C) that many MoS₂ nanoflowers are linked together with the

AgVO₃ nanorods. However, the MoS₂ nanoflowers in direct contact with the AgVO₃ nanorods were not dislodged, thereby ensuring that the AgVO₃/MoS₂ heterojunction existed stably throughout the degradation process. This was also the main reason for the negligibly small reduction in photocatalyst activity after the fourth cycle experiment.

3.2.4. Intermediates and mineralization ability test

The degradation intermediates of TC over the 3%-AgVO₃/MoS₂ was investigated by examining the HPLC-MS results. The corresponding changes in the characteristic peak of TC ($m/z = 445$) became increasingly smaller, and some additional peaks appear in Fig. S3. This illustrates that the TC had been decomposed into other intermediate products and these

Fig. 8. (A) Cycling experiments for the photocatalytic degradation of TC by the as-prepared 3%-AgVO₃/MoS₂ under visible irradiation; (B) XRD patterns of 3%-AgVO₃/MoS₂ before (a) and after (b) photocatalytic degradation of TC for the fourth cycle; TEM of 3%-AgVO₃/MoS₂ before (C) and after (D) photocatalytic degradation of TC for the fourth cycle.

Fig. 9. Possible intermediate products resulting from the degradation of TC.

substances were gradually decomposed to CO_2 , H_2O , and other small molecules. As shown in Fig. 9, the prominent anion with m/z of 445 is the deprotonated tetracycline molecular ion, showing that the tetracycline was fragmented into small molecules during the process of degradation [45]. It was found that the intermediate product A ($m/z = 362$) was obtained by breaking the naphthalene ring under alkaline conditions [46] to obtain the lactone structure product B ($m/z = 361$) by the formation of hydroxyl electron-rich groups (negative oxygen ions). This product undergoes a nucleophilic reaction with carbonyl to become product C ($m/z = 318$) by losing N-methyl groups. Furthermore, another degradation pathway involved the fragmentation of tetracycline into product D ($m/z = 345$) by losing the leaving groups of $-\text{CH}_3$, $-\text{N}(\text{CH}_3)_2$ and $-\text{CO}(\text{NH}_2)$ to become product E ($m/z = 329$) by losing $-\text{OH}$. This product decomposed into product F ($m/z = 274$) through ring-opening reactions [47]. Finally, the tetracycline was gradually broken down into small molecules as the photocatalytic reactions progressed.

3.3. Role of AgVO_3 in the $\text{AgVO}_3/\text{MoS}_2$ composites

Generally, the catalytic performance had two key properties: (1) the separation efficiency of charge carriers and (2) the application of an electron-hole mechanism in the production of ROSs [48]. In terms of the first, the separation efficiency of charge carriers can always be reflected by measuring the EIS and PL. The interfacial charge transfer resistance and optical carrier separation efficiency were measured by EIS [49], where a smaller radius indicates higher charge transfer efficiency [50, 51]. Fig. 10(A) shows that the radius of 3%- $\text{AgVO}_3/\text{MoS}_2$ particles is smaller than that of pure MoS_2 , indicating that adding AgVO_3 could improve the separation efficiency of charge carriers.

It is well known that the peak intensity obtained by PL emission spectroscopy indirectly reflects the separation efficiency of charge carriers. The emission of photoluminescence by semiconductor materials originating from the radiative recombination of photo-generated electrons and holes, as well as

Table 3

Corresponding calculation results for radiative lifetime of the fitting decay curves.

Sample	A_1	τ_1	A_2	τ_2	τ_{ave}
MoS_2	1326.32	0.95	1326.32	0.95	0.95 ns
AgVO_3	928.69	1.30	928.69	1.30	1.30 ns
3%- $\text{AgVO}_3/\text{MoS}_2$	252.29	8.00	3491.75	0.83	1.32 ns

two major photo-physical processes, could produce photoluminescence signals [52]. The lower PL intensity represented a reduced electron-hole recombination rate and superior photocatalytic activity [53–55]. Fig. 10(B) shows the PL spectra of AgVO_3 , MoS_2 , and 3%- $\text{AgVO}_3/\text{MoS}_2$. The emission spectrum of MoS_2 has the highest intensity with the peak located at 468 nm. However, the PL intensity of 3%- $\text{AgVO}_3/\text{MoS}_2$ significantly decreased when AgVO_3 was added, further demonstrating that the recombination of photogenerated electron-hole pairs was suppressed owing to the addition of AgVO_3 . In addition, the time-resolved fluorescence decay spectra were also recorded. The fitted time-resolved fluorescence emission decay spectra are shown in Fig. 10(C). The time-resolved fluorescence decay curves of AgVO_3 , MoS_2 , and 3%- $\text{AgVO}_3/\text{MoS}_2$ were fitted by the bi-exponential function:

$$I(t) = A_1 \times \exp\left(\frac{-t}{\tau_1}\right) + A_2 \times \exp\left(\frac{-t}{\tau_2}\right) \quad (4)$$

and the average lifetime was calculated by

$$\tau_{ave} = \frac{(A_1\tau_1 + A_2\tau_2)}{(A_1 + A_2)} \quad (5)$$

where $I(t)$ is the PL intensity at a certain delay time, A_1 and A_2 represent the relative weight of the decay components at $t = 0$ [56]. Table 3 lists the radiative lifetime of the fitted decay curves of MoS_2 , AgVO_3 , and the 3%- $\text{AgVO}_3/\text{MoS}_2$ heterojunction, which were 0.95, 1.30, and 1.32 ns, respectively. The increase in decay lifetime of 3%- $\text{AgVO}_3/\text{MoS}_2$ could be explained by the introduction of AgVO_3 , which increased the O_2 adsorption/activation and accelerated the consumption of photo-excited electrons. The participation of additional electrons in the degradation process could enhance the photocatalytic effi-

Fig. 10. EIS curves (A), solid PL emission spectra (B) and time-resolved fluorescence decay curves (C) of the AgVO_3 , MoS_2 , and 3%- $\text{AgVO}_3/\text{MoS}_2$.

Fig. 11. DMPO spin-trapping ESR spectra recorded with MoS₂ and 3%-AgVO₃/MoS₂ samples in the dark and under visible light irradiation at ambient temperature (A, B) DMPO-•OH in aqueous dispersion; (C, D) DMPO-O₂•⁻ in methanol dispersion.

ciency.

In terms of the second key property, combining AgVO₃ with MoS₂ could increase the ROSs production. To provide evidence for this, an electron spin resonance (ESR) spin-trap technique was used for •O₂⁻ and •OH detection with 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO), and the H₂O₂ yield was determined by using *p*-hydrophenylacetic acid (POPHA) [57]. In Fig. 11(A) and (B), none of the characteristic signals of the DMPO-•OH and DMPO-O₂•⁻ were observed in the dark; thus, it could be concluded that the formation of O₂•⁻ and •OH on the as-prepared samples would require irradiation by light. In Fig. 11(C), the characteristic peaks of the DMPO-•OH adduct were only observed on 3%-AgVO₃/MoS₂ in the presence of light. However, in Fig. 11(D), the characteristic peaks of the DMPO-O₂•⁻ adduct were observed both for the pure MoS₂ and 3%-AgVO₃/MoS₂ composite photocatalysts. Moreover, it was obvious that the intensities of both the DMPO-•OH and DMPO-O₂•⁻ signals of the 3%-AgVO₃/MoS₂ composite were much higher than that of MoS₂, respectively. These results reveal that the introduction of AgVO₃ could enhance the formation of O₂•⁻ and •OH species. In addition to the direct determination of ROSs by ESR tests, indirect analysis by the addition of scavengers was also conducted in this study. Triethanolamine (TEOA), isopropanol (IPA), and benzoquinone (BQ) were

used as scavengers for holes (h⁺), hydroxyl radicals (•OH), and superoxide radicals (•O₂⁻), respectively. As shown in Fig. S4, under visible light irradiation, the degradation effect of TC decreased slightly from 73% to 69.2% after adding BQ. In contrast, the TC degradation rate was largely reduced to 61.7% and 45% upon addition of TEOA and IPA, respectively. The above results enabled us to conclude that the species •O₂⁻, h⁺, and •OH all took part in the process of photocatalytic degradation.

To further investigate that the addition of AgVO₃ could increase the generation of ROSs under UV light irradiation, a POPHA fluorescence method was employed to investigate the generation of H₂O₂ from different photocatalysts and further examine the pathway of molecular oxygen activation [58]. Fig. 12 shows that significantly more H₂O₂ was generated over 3%-AgVO₃/MoS₂ than over MoS₂, which was attributed to increased H₂O₂ generation because of the addition of AgVO₃. The amount of H₂O₂ generated by the 3%-AgVO₃/MoS₂ composite photocatalyst increased with prolonged exposure to light, but almost no H₂O₂ was generated in the dark after 30 min; thus, one of the necessary conditions for the production of ROSs was irradiation by light. This result also indicated that H₂O₂ was generated via a two-electron reduction of O₂ during photocatalytic degradation (O₂ + 2H⁺ + 2e⁻ = H₂O₂, 0.682 V vs. NHE) [59].

Fig. 12. Fluorescence spectra of H_2O_2 generation curves of different samples: 3%- $\text{AgVO}_3/\text{MoS}_2$ exposed to light for 3 h (a), 2 h (b), 1 h (c), and in the dark (d); MoS_2 exposed to light for 3 h (e), 2 h (f), 1 h (g), and in the dark (h).

3.4. Possible photocatalytic reaction mechanism

The photocatalytic activities depended on the migration, transfer, and separation of photogenerated charge carriers and the band positions of AgVO_3 and MoS_2 also determined the migration path of electrons and holes. The conduction band edge (E_{CB}) was calculated by the following empirical equation:

$$E_{\text{VB}} = X - E^e + 0.5E_g \quad (6)$$

$$E_{\text{CB}} = E_{\text{VB}} - E_g \quad (7)$$

where X is the absolute electronegativity of the semiconductor, which is the geometric mean of the electronegativity of the constituent atoms, E^e is the energy of free electrons on the hydrogen scale (4.5 eV), and E_g is the band gap of the semiconductor that can be obtained from Fig. S2, and the valence band edge (E_{VB}) can be determined by $E_{\text{VB}} = E_{\text{CB}} + E_g$ [60,61]. As shown in Fig. 13, the densities of the total states of the MoS_2 and AgVO_3 valence band were measured to be 1.70 and 2.49 eV, respectively. The band gaps of MoS_2 and AgVO_3 acquired from the DRS analysis were 1.79 and 2.18 eV, respectively. Therefore, the E_{CB} values of MoS_2 and AgVO_3 were -0.09 and 0.31 eV, respectively. According to the band energy structure, the pho-

Fig. 14. Proposed mechanism of photocatalytic reaction over the 3%- $\text{AgVO}_3/\text{MoS}_2$ system.

togenerated electrons from the CB of MoS_2 were transferred to the CB of AgVO_3 , while the photogenerated holes from the VB of AgVO_3 were transferred to the VB of MoS_2 , which allowed for more effective charge separation.

Based on the observed photocatalytic activity and the characterization presented above, we conclude that a two-electron process and the surface modification by AgVO_3 facilitated the O_2 adsorption/activation for $\cdot\text{OH}$ and H_2O_2 production, thus enhancing the photocatalytic activity. The mechanistic pathway is illustrated in Fig. 14. According to the DRS results, the band gap of MoS_2 was as narrow as 1.79 eV (Fig. S2), which indicated the charge carriers generated by MoS_2 underwent facile recombination. Therefore, only few of the electrons photogenerated by the MoS_2 could react with the dissolved oxygen and, because of the difficulty of O_2 adsorption/activation, these unreacted electrons were often recombining with holes. However, when AgVO_3 was deposited on the surface of MoS_2 , the advantageous O_2 adsorption/activation property of the AgVO_3 would improve the oxygen reduction reaction on the MoS_2 surface. This would enhance the production of ROSs via electronic consumption, leaving a larger number of holes for the degradation of organic pollutants. The reaction process can be represented by Eqs. (8)–(15). The combination of ESR and capture experiments determined (13), (14) to be the main mechanistic pathway.

Fig. 13. Valence band XPS spectra of MoS_2 (A) and AgVO_3 (B).

4. Conclusions

In summary, we successfully prepared a highly efficient $\text{AgVO}_3/\text{MoS}_2$ composite photocatalyst by a hydrothermal method. The as-prepared 3%- $\text{AgVO}_3/\text{MoS}_2$ composite achieved the best performance toward the degradation of different organic pollutants compared to pure MoS_2 . The enhanced photocatalytic performance was attributed to the specific catalytic properties of AgVO_3 , which effectively promote the formation of adsorbed O_2 to ROSs on the surface of the 3%- $\text{AgVO}_3/\text{MoS}_2$ composite, thus greatly improving the photocatalytic activity. Simultaneously, the effective consumption of photo-generated electrons on the AgVO_3 surface leaves behind more holes for the degradation of pollutants. This study provided new insights into the rational design of composite photocatalysts to promote the generation of ROSs by surface catalysis engineering and may be put into practice in environmental governance.

References

- [1] L. Wollenberger, B. Halling-Sørensen, K. O. Kusk, *Chemosphere*, **2000**, 40, 723–730.
- [2] J. L. Martinez, *Environ. Pollut.*, **2009**, 157, 2893–2902.
- [3] J. Zhang, X. H. Mao, W. Xiao, Y. F. Zhuang, *Chin. J. Catal.*, **2017**, 38, 2009–2020.
- [4] R. Schloegl, *Nat. Mater.*, **2008**, 7, 772–774.
- [5] A. Kudo, Y. Miseki, *Chem. Soc. Rev.*, **2009**, 38, 253–278.
- [6] H. Tong, S. Ouyang, Y. Bi, N. Umezawa, M. Oshikiri, J. Ye, *Adv. Mater.*, **2012**, 24, 229–251.
- [7] Z. Y. Lu, Z. Zhu, D. D. Wang, Z. F. Ma, W. D. Shi, Y. S. Yan, X. X. Zhao, H. J. Dong, L. Yang, Z. F. Hua, *Catal. Sci. Technol.*, **2016**, 1367–1377.
- [8] W. W. He, H. M. Jia, D. F. Yang, P. Xiao, X. L. Fan, Z. Zheng, H. K. Kim, W. G. Wamer, J. J. Yin, *ACS Appl. Mater. Interfaces*, **2015**, 7, 16440–16449.
- [9] S. J. Liu, F. T. Li, Y. L. Li, Y. J. Hao, X. J. Wang, B. Li, R. H. Liu, *Appl. Catal. B*, **2017**, 212, 115–128.
- [10] C. R. Chang, Z. Q. Huang, J. Li, *Nano Res.*, **2015**, 8, 3737–3748.
- [11] C. S. Hinde, D. Ansovini, P. P. Wells, G. Collins, S. V. Aswegen, J. D. Holmes, T. S. A. Hor, R. Raja, *ACS Catal.*, **2015**, 6, 3807–3816.
- [12] H. Tong, S. X. Ouyang, Y. P. Bi, N. T. Umezawa, M. Oshikiri, J. H. Ye, *Adv. Mater.*, **2012**, 24, 229–251.
- [13] V. R. Raja, D. R. Rosalinne, A. Suganthi, M. Rajarajan, *Solid State Sci.*, **2017**, 67, 99–108.
- [14] H. Peng, J. Lu, C. X. Wu, Z. X. Yang, H. Chen, W. J. Song, P. Q. Li, H. Z. Yin, *Appl. Surf. Sci.*, **2015**, 353, 1003–1012.
- [15] S. V. P. Vattikuti, C. Byon, *Superlattice. Microsc.*, **2016**, 100, 514–525.
- [16] Z. Y. Lu, F. Chen, M. He, M. S. Song, Z. F. Ma, W. D. Shi, Y. S. Yan, Z. J. Lan, F. Li, P. Xiao, *Chem. Eng. J.*, **2014**, 249, 15–26.
- [17] H. Hussain, G. Tocci, T. Woolcot, X. Torrelles, C. L. Pang, D. S. Humphrey, C. M. Yim, D. C. Grinter, G. Cabailh, O. Bikondoa, R. Lindsay, J. Zegenhagen, A. Michaelides, G. Thornton, *Nat. Mater.*, **2017**, 16, 461–466.
- [18] W. W. He, H. K. Kim, W. G. Wamer, D. Melka, J. H. Callahan, J. J. Yin, *J. Am. Chem. Soc.*, **2014**, 136, 750–757.

Graphical Abstract

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Enhanced photocatalytic performance of MoS_2 modified by AgVO_3 from improved generation of reactive oxygen species

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The $\text{AgVO}_3/\text{MoS}_2$ composite photocatalyst was synthesized by the hydrothermal method. The excellent photocatalytic performance was due to the modification of MoS_2 by AgVO_3 which facilitated the O_2 adsorption/activation and accelerated the two-electron oxygen reduction reaction for H_2O_2 generation on the surface of MoS_2 .

- [19] R. Abazari, A. R. Mahjoub, *Ind. Eng. Chem. Res.*, **2017**, 56, 623–634.
- [20] H. F. Shi, Z. S. Li, J. H. Kou, J. H. Ye, Z. G. Zou, *J. Phys. Chem. C*, **2011**, 115, 145–151.
- [21] J. H. Yi, J. X. Song, H. M. Mo, Y. P. Yang, *Adv. Powder Technol.*, **2018**, 29, 319–324.
- [22] C. M. Huang, G. T. Pan, Y. C. M. Li, M. H. Li, T. C. K. Yang, *Appl. Catal. B*, **2009**, 358, 164–172.
- [23] Z. J. Chen, S. K. Gao, R. H. Li, M. D. Wei, K. M. Wei, H. S. Zhou, *Electrochim. Acta*, **2008**, 53, 8134–8137.
- [24] L. Q. Mai, L. Xu, Q. Gao, C. H. Han, B. Hu, Y. Q. Pi, *Nano Lett.*, **2010**, 10, 2604–2608.
- [25] X. H. Wang, J. Yang, S. Q. Ma, D. Zhao, J. Dai, D. F. Zhang, *Catal. Sci. Technol.*, **2016**, 6, 243–253.
- [26] H. D. Lu, J. X. wang, Z. Y. Du, Y. P. Liu, M. Li, P. Chen, L. Z. Zhang, *Mater. Lett.*, **2015**, 157, 231–234.
- [27] W. Zhao, J. H. Li, Z. B. Wei, S. M. Wang, H. He, C. Sun, S. G. Yang, *Appl. Catal. B*, **2015**, 179, 9–20.
- [28] L. Cao, *Mater. Lett.*, **2017**, 188, 252–256.
- [29] H. Y. Li, J. Li, C. C. Xu, P. Yang, D. H. L. Ng, P. Song, M. Zuo, *J. Alloys Compd.*, **2017**, 698, 852–862.
- [30] Y. Pei, T. Fan, H. Chu, Y. C. Ge, Y. Yang, P. Dong, R. Baines, M. X. Ye, J. F. Shen, *J. Alloys Compd.*, **2017**, 724, 1014–1022.
- [31] X. Zhang, J. Zhang, J. Q. Yu, Y. Zhang, Z. X. Cui, Y. Sun, B. R. Hou, *Appl. Catal. B*, **2018**, 220, 57–66.
- [32] Y. K. Kim, D. H. Min, *Nanoscale*, **2013**, 5, 3638–3642.
- [33] H. J. Cheng, J. G. Hou, O. Takeda, X. M. Guo, H. M. Zhu, *J. Mater. Chem A*, **2015**, 3, 11006–11013.
- [34] B. Chai, C. Liu, C. L. Wang, J. T. Yan, Z. D. Ren, *Chin. J. Catal.*, **2017**, 38, 2067–2075.
- [35] Y. D. Hou, A. B. Laursen, J. S. Zhang, G. G. Zhang, Y. S. Zhu, X. C. Wang, S. Dahl, I. Chorkendorff, *Angew. Chem. Int. Ed.*, **2013**, 52, 3621–3625.
- [36] L. F. Li, X. L. Zhao, D. L. Pan, G. S. Li, *Chin. J. Catal.*, **2017**, 38, 2132–2140.
- [37] T. Xiong, F. Dong, Z. Wu, *RSC Adv.*, **2014**, 4, 56307–56312.
- [38] C. S. Zhu, L. Zhang, B. Jiang, J. T. Zheng, P. Hu, S. J. Li, M. B. Wu, W. T. Wu, *Appl. Surf. Sci.*, **2016**, 377, 99–108.
- [39] Z. D. Lei, J. J. Wang, L. Wang, X. Y. Yang, G. Xu, L. Tang, *J. Hazard. Mater.*, **2016**, 312, 298–306.
- [40] X. J. Wen, C. G. Niu, L. Zhang, G. M. Zeng, *Dalton Trans.*, **2017**, 46, 4982–4993.
- [41] M. Rahman, K. Davey, S. Z. Qiao, *Small*, **2017**, 23, 1700376.
- [42] X. L. Yin, L. L. Li, W. J. Jiang, Y. Zhang, X. Zhang, L. J. Wan, J. S. Hu, *ACS Appl. Mater. Interfaces*, **2016**, 8, 15258–15266.
- [43] W. K. Ho, J. C. Yu, J. Lin, J. G. Yu, P. S. Li, *Langmuir*, **2014**, 2004, 5865–5869.
- [44] M. Özacar, *Adsorption*, **2003**, 9, 125–132.
- [45] Z. F. Ye, J. Z. Li, M. J. Zhou, H. Q. Wang, Y. Ma, P. W. Huo, L. B. Yu, Y. S. Yan, *Chem. Eng. J.*, **2016**, 304, 917–933.
- [46] X. D. Zhu, Y. J. Wang, R. J. Sun, D. M. Zhou, *Chemosphere*, **2013**, 92, 925–932.
- [47] M. H. Cao, P. F. Wang, Y. H. Ao, C. Wang, J. Hou, J. Qian, *J. Colloid Interf. Sci.*, **2016**, 467, 129–139.
- [48] J. H. Yang, D. G. Wang, H. X. Han, C. Li, *Acc. Chem. Res.*, **2013**, 46, 1900–1909.
- [49] Q. P. Xu, R. Z. Li, C. D. Wang, D. Yuan, *J. Alloys Compd.*, **2017**, 723, 441–447.
- [50] B. J. Ng, L. K. Putri, L. L. Tan, P. Pasbakhsh, S. P. Chai, *Chem. Eng. J.*, **2017**, 316, 41–49.
- [51] M. Yan, Y. L. Wu, F. F. Zhu, Y. Q. Hua, W. D. Shi, *Phys. Chem. Chem. Phys.*, **2016**, 4, 3308–3315.
- [52] C. M. Yang, G. M. Gao, J. J. Zhang, R. P. Liu, R. C. Fan, M. Zhao, Y. W. Wang, S. C. Gan, *Phys. Chem. Chem. Phys.*, **2017**, 22, 14431–14444.
- [53] S. Liu, M. Q. Yang, Z. R. Tang, Y. J. Xu, *Nanoscale*, **2014**, 6, 7193–7198.
- [54] R. Wang, L. Cao, *J. Alloys Compd.*, **2017**, 722, 445–451.
- [55] Y. J. Ma, Z. M. Wang, X. F. Xu, J. Y. Wang, *Chin. J. Catal.*, **2017**, 38, 1956–1969.
- [56] J. B. Chen, H. N. Che, K. Huang, C. B. Liu, W. D. Shi, *Appl. Catal. B*, **2016**, 192, 134–144.
- [57] J. Di, J. X. Xia, M. X. Ji, B. Wang, X. W. Li, Q. Zhang, Z. G. Chen, H. M. Li, *ACS Sustainable Chem. Eng.*, **2016**, 4, 136–146.
- [58] K. Zhao, L. Zhang, J. Wang, Q. Li, W. He, J. J. Yin, *J. Am. Chem. Soc.*, **2013**, 135, 15750–15753.
- [59] P. Wang, Y. Xia, P. Wu, X. Wang, H. Yu, J. Yu, *J. Phys. Chem. C*, **2014**, 118, 8891–8898.
- [60] K. Fan, Z. L. Jin, H. Yuan, H. Y. Hu, Y. P. Bi, *Chin. J. Catal.*, **2017**, 38, 20156–2066.
- [61] S. H. Liu, W. T. Tang, W. X. Lin, *Int. J. Hydrogen Energy*, **2017**, 42, 24006–24013.

利用AgVO₃改性MoS₂增强活性氧产生及其光催化性能的提高

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摘要: 随着全球工业化进程的发展, 环境污染问题日益严重, 已经成为21世纪影响人类生存与发展的重要问题. 光催化氧化技术被认为是解决环境问题最有应用前景的技术之一, 已经成为环境领域的研究热点. 众所周知, 二硫化钼(MoS₂)可以被可见光激发产生电子-空穴对, 但是由于其氧化还原电势并不高, 抑制了氧分子活化的量子效率, 且激发后的光生载流子容易复合, 导致光催化效率不高. 因此, 迫切需要对MoS₂光催化材料进行修饰与改性, 采用提高光催化过程中活性氧(ROS)的量来提高其光催化活性. 银钒氧化物(AgVO₃, Ag₂V₄O₁₁, Ag₃VO₄和Ag₄V₂O₇等)因其在锂电池、传感器和光催化剂领域的应用而引起了人们的关注. 其中, AgVO₃具有较窄的带隙和高度分散的价带, 具有潜在的应用价值.

本文采用水热法成功制备了AgVO₃/MoS₂复合光催化剂, 并采用X射线粉末衍射、扫描电子显微、透射电子显微镜和紫外-可见漫反射光谱等表征技术研究了所制光催化剂的物相结构、样品形貌和光学性能. 以四环素为研究对象, 将其应用

于 $\text{AgVO}_3/\text{MoS}_2$ 复合光催化剂的降解实验. 结果表明, 随着 AgVO_3 质量比从1.0 wt%增加到3.0 wt%, 所得催化剂的光催化活性不断提高; 当进一步增加 AgVO_3 的质量时, 复合催化剂的活性逐渐降低. 这是由于过多的 AgVO_3 的引入导致在光催化剂表面形成电子-空穴对复合中心, 增加了载流子复合几率. 因此, $\text{AgVO}_3/\text{MoS}_2$ 复合光催化剂中 AgVO_3 的最佳质量比为3.0 wt%, 其降解速率常数为 0.0087 min^{-1} , 分别是 MoS_2 (0.00509 min^{-1})和 AgVO_3 (0.00495 min^{-1})的1.71和1.76倍. 由于 AgVO_3 改性后的 MoS_2 具有优异的光催化性能, 能促进 O_2 的吸附/活化, 加速 MoS_2 表面生成 H_2O_2 的双电子氧还原反应, 从而产生更多的ROSs. 利用电子自旋共振光谱、POPHA荧光检测和自由基捕获实验相结合的方法来阐明ROSs的形成机理. 同时, ROSs的产生会加速消耗 AgVO_3 导带上的电子, 为降解污染物留下更多的空穴. 本文为表面催化工程促进ROSs生成的合理设计提供了新的思路, 有望在环境治理中得到实际应用.

关键词: 活性氧物种; $\text{AgVO}_3/\text{MoS}_2$; 光催化剂; 可见光; 有机污染物

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