Rodlike AgI/Ag$_2$Mo$_2$O$_7$ Heterojunctions with Enhanced Visible-Light-Driven Photocatalytic Activity

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ABSTRACT: Novel AgI/Ag$_2$Mo$_2$O$_7$ heterojunctions were prepared by reacting Ag$_2$Mo$_2$O$_7$ microrods with an aqueous KI solution at room temperature. The composite materials, compared with neat AgI and Ag$_2$Mo$_2$O$_7$, showed much higher activities in the photocatalytic degradation of aqueous rhodamine B, methyl orange, tetracycline hydrochloride, and levofloxacin solutions under visible-light irradiation. The structures, morphologies, and other physicochemical properties of AgI, Ag$_2$Mo$_2$O$_7$, and AgI/Ag$_2$Mo$_2$O$_7$ composites were studied via various characterization techniques. The active species involved in the photocatalytic process were examined via radical-capturing experiments and electron spin resonance. Superoxide anion radicals (O$_2^−$) and photogenerated holes (h$^+$) were found to be the main active species. Photocatalytic mechanisms were proposed and reasons for the enhanced photocatalytic activity were explained.

1. INTRODUCTION

Heterogeneous catalysis plays a key role in removing environmental pollutants in waste gases, indoor air, or waste water, whereas photocatalysis by semiconductors is a key branch of environmental catalysis research.¹⁻³ TiO$_2$, the benchmark photocatalyst, relies heavily on ultraviolet (UV) light that occupies only a very small portion of the sun light. To make full use of visible light that represents a lion share of sunlight, novel visible-light responsive photocatalysts are especially needed.

There are many types of visible-light-responsive photocatalysts. In particular, Ag-containing compounds such as AgX (X = Cl, Br, or I),⁴ Ag$_2$O,⁵ Ag$_3$VO$_4$,⁶ Ag$_2$CO$_3$,⁷ Ag$_3$PO$_4$,⁸ and Ag$_2$CrO$_4$,⁹ have attracted much attention.¹⁰ Among these Ag-containing photocatalysts, Ag$_2$MoO$_4$ has aroused great interest due to its electronic structure and catalytic mechanisms were proposed.

Nevertheless, there are only a few studies on Ag$_2$Mo$_2$O$_7$-based heterojunctions such as AgO/Ag$_2$Mo$_2$O$_7$,¹⁴ g-C$_3$N$_4$/m-Ag$_2$Mo$_2$O$_7$,²⁰ Ag$_2$Mo$_2$O$_7$/AgBr−Ag,²¹ and Ag$_2$PO$_4$/Ag/Ag$_2$MoO$_4$.²² Ag$_2$MoO$_4$, with excellent visible-light response and good photocatalytic degradation activity,²³⁻²⁴ has been used to construct heterojunction photocatalysts such as Ag$_2$VO$_4$/AgI,²⁵,²⁶ Ag$_2$O/AgI,²⁷ Ag$_2$WO$_4$/AgI,²⁸ AgI/g-C$_3$N$_4$,²⁹ AgI/Bi$_2$MoO$_6$,³⁰ AgI/BiVO$_4$,³¹ AgI/BiOBr,³² and AgI/BiOCOOH.³³ However, to the best of our knowledge, AgI/Ag$_2$Mo$_2$O$_7$ has not been reported.

Herein, Ag$_2$Mo$_2$O$_7$ microrods were prepared via a facile hydrothermal process,³⁰ and AgI particles were then deposited onto Ag$_2$Mo$_2$O$_7$ surfaces via treating Ag$_2$Mo$_2$O$_7$ in an aqueous KI solution (Scheme 1). Similar treatment processes were used to prepare Ag$_2$Mo$_2$O$_7$/AgBr−Ag by reacting Ag$_2$Mo$_2$O$_7$ with an aqueous NaBr solution and AgI/Ag$_2$VO$_3$ by reacting Ag$_2$VO$_3$ with an aqueous KI solution.³⁵ Interestingly, AgI/Ag$_2$Mo$_2$O$_7$ showed a much higher photocatalytic activity than neat AgI and Ag$_2$MoO$_4$. The materials were characterized and tested in visible-light-driven photocatalysis. Possible photocatalytic mechanisms were proposed.

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2. RESULTS AND DISCUSSION

2.1. Characterization of the Samples. Figure 1 shows the X-ray diffraction (XRD) patterns of AgI, Ag₂Mo₂O₇, and S5. The XRD patterns of pure AgI and Ag₂Mo₂O₇ are consistent with the standard XRD data of hexagonal phase AgI (JCPDS No. 09-0374) and monoclinic phase Ag₂Mo₂O₇ (ICSD No. 15-4826), respectively. Compared with pure Ag₂Mo₂O₇, S5 shows distinctive peaks at 2θ = 22.3, 23.7, 25.4, 32.8, 39.2, 42.7, and 46.3°, corresponding to the (100), (002), (101), (102), (110), (103), and (112) planes of hexagonal AgI, respectively. The data mean that S5 contains both Ag₂Mo₂O₇ and AgI. Moreover, with the increasing AgI contents in AgI/Ag₂Mo₂O₇ (S1–S5), the intensity of the AgI peaks enhances gradually, whereas the intensity of the Ag₂Mo₂O₇ peaks becomes weaker (Figure S1). No impurity phases are detected.

The compositions and chemical status of the as-prepared catalysts were analyzed by X-ray photoelectron spectroscopy (XPS). The XPS survey scan spectrum in Figure S2 reveals that S5 contains Ag, I, Mo, O, and adventitious C. The peak position of C 1s at 284.6 eV is used to calibrate the position of other elements. The high-resolution XPS scan spectra of Ag 3d, I 3d, Mo 3d, and O 1s are exhibited in Figure 2. For S5, the element Ag is present in the form of Ag⁺, corresponding to the binding energies of 373.8 and 367.8 eV for Ag 3d₃/₂ and Ag 3d₅/₂, respectively. Figure 2b shows two peaks at 619.6 eV (I 3d₅/₂) and 631.0 eV (I 3d₃/₂) attributed to I⁻ in S5. Two distinct peaks at 232.1 and 235.3 eV (corresponding to Mo⁶⁺) are seen in the Mo 3d high-resolution spectra (Figure 2c). As shown in Figure 2d, the high-resolution O 1s peak of S5 is deconvoluted into three peaks at binding energies of 530.2, 531.5, and 533.3 eV, corresponding to Mo–O–Mo bonds, oxygen vacancy, and adsorbed oxygen on the surface of the sample, respectively. Notably, Ag 3d and I 3d peaks in S5 move...
to a positive position compared with those in AgI, whereas the peak of Mo 3d in S5 shifts slightly to lower binding energies compared with that in Ag₂Mo₂O₇. All the shifts in the XPS spectra can be ascribed to the intense interaction between closely contacted phases of AgI and Ag₂Mo₂O₇.⁵⁶

Figure 3 depicts the scanning electron microscopy (SEM) images of Ag₂Mo₂O₇, AgI, and S5. Pure Ag₂Mo₂O₇ shows a microrod morphology with a mean diameter of 1–2 μm (Figure 3a,b), whereas pure AgI consists of many irregular particles with sizes of about 10 μm (Figure 3c,d). For S5 (Figure 3e,f), the Ag₂Mo₂O₇ microrods are decorated by numerous AgI particles with a grain size of about 100 nm. The reason for the difference seen in the sizes of pure AgI and AgI particles on Ag₂Mo₂O₇ microrods is that pure AgI is formed by direct precipitation in the solution (the growth of AgI crystal is out of control), whereas AgI/Ag₂Mo₂O₇ is produced by reaction between Ag₂Mo₂O₇ microrods and aqueous KI at the liquid–solid interface (this conversion is supposed to be more difficult). As seen from Figure S3, the amount of AgI particles assembled on the surface of Ag₂Mo₂O₇ increases with enhanced content of AgI (Figure S3). The energy-dispersive spectrometry (EDS) result in Figure S4 also indicates the coexistence of Ag, I, Mo, and O elements in S5. The molar percentage of I element is shown to be 21.4%, in line with the theoretical content of 21.1%.

The N₂ adsorption–desorption isotherms of Ag₂Mo₂O₇, AgI, and S5 were measured. In Figure S5, S5 shows the isotherms of type IV with a type H₃ hysteresis loop (based on IUPAC classification) at high relative pressures (p/p₀) between 0.85 and 1.0, suggesting the presence of aggregation voids between the particles.⁵⁷ For comparison, Ag₂Mo₂O₇ and AgI exhibit type II isotherms without a significant hysteresis loop, indicating there are no pores in Ag₂Mo₂O₇ and AgI.⁵⁸ The Brunauer–Emmett–Teller (BET) surface areas of Ag₂Mo₂O₇, AgI, and S1–S5 are 1.43, 0.93, 1.87, 2.07, 4.31, 5.86, and 5.89 m²/g, respectively. Among them, S5 shows the highest BET surface areas.
Figure 4 shows the transmission electron microscopy (TEM) results of Ag$_2$Mo$_2$O$_7$, AgI, and S5. Compared with the pure Ag$_2$Mo$_2$O$_7$ microrod (Figure 4a), the surface of S5 (Figure 4c) becomes rougher due to some small bulges observed at the microrod surface, which can be recognized as AgI particles, in line with the SEM images (Figure 3). The high-resolution TEM (HRTEM) image of S5 is presented in Figure 4d. The lattice fringes of 0.398 and 0.373 nm correspond to the (100) and (002) lattice planes of AgI, whereas the lattice fringes of 0.321 and 0.286 nm are attributed to the (022) and (200) lattice planes of Ag$_2$Mo$_2$O$_7$. The results prove the formation of a heterojunction structure in S5.

The distribution of elements in S5 was demonstrated by scanning transmission electron microscopy (STEM)−energy-dispersive X-ray (EDX) elemental mapping. As shown in Figure 5, the Ag, Mo, and I elements are all uniformly distributed in S5. In particular, the distribution of I element is wider than that of the Mo element, indicating that the Ag$_2$Mo$_2$O$_7$ microrod is well covered by AgI particles, consistent with the SEM (Figure 3) and TEM (Figure 4) observations.

The optimal properties of the samples were investigated by UV−vis diffuse reflectance spectroscopy (Figure 6a). Pure Ag$_2$Mo$_2$O$_7$ and AgI present a broad absorbance in both ultraviolet and visible-light ranges. The optical absorption edges of pure Ag$_2$Mo$_2$O$_7$ and AgI are located at 455 and 440 nm, respectively. S5 exhibits light absorption edges between 455 and 440 nm. This result indicates that all of the photocatalysts possess visible-light response. However, the light absorption ability of the samples (above 450 nm) clearly follows the sequence of Ag$_2$Mo$_2$O$_7$ > S5 > AgI. In addition, the optical absorption edges of AgI/Ag$_2$Mo$_2$O$_7$ show a slight red shift with the increasing content of AgI (Figure S6).

The band gap energies ($E_g$) of pure Ag$_2$Mo$_2$O$_7$ and AgI are calculated according to the following equation:

$$a h \nu = A(h \nu - E_g)^{n/2}$$

(1)

where $a$, $A$, $h \nu$, and $E_g$ are the absorption coefficient, proportionality constant, photon energy, and band gap energy, respectively. The value of index $n$ is determined by the type of optical transition of semiconductors; $n$ equals to 1 for the direct transition and 4 for the indirect transition of photocatalysts. The optical transition of AgI is direct, and the $E_g$ of AgI is estimated from the plot of $(a h \nu)^2$ versus the photon energy ($h \nu$) to be 2.82 eV. Ag$_2$Mo$_2$O$_7$ is an indirect semiconductor, so the value of $n$ is 4 and the $E_g$ is measured to be 2.68 eV (Figure 6b).

The conduction band (CB) and valence band (VB) positions can be determined through the following empirical equations:

$$E_{VB} = X - E_0 + 0.5E_g$$

(2)

$$E_{CB} = E_{VB} - E_g$$

(3)

where $E_{VB}$ is the VB edge potential and $X$ is the absolute electronegativity of the semiconductor. The $X$ values for Ag$_2$Mo$_2$O$_7$ and AgI are 6.08 V$^{40}$ and 5.48 V$^{45}$, respectively. $E_0$ is the energy of free electrons on the hydrogen scale, with the value of 4.5 V$^{49}$ and $E_g$ is the band gap energy of the semiconductor. The $E_{VB}$ values of Ag$_2$Mo$_2$O$_7$ and AgI are calculated to be 2.92 and 2.39 V vs normal hydrogen electrode (NHE), and the corresponding $E_{CB}$ values are calculated to be 0.24 and −0.42 V vs NHE, respectively.

2.2. Photocatalytic Activities of Samples. The photocatalytic activities of the samples were first measured by degrading aqueous solution of methyl orange (MO) under visible-light irradiation. Figure 7a shows the variations of MO...
concentration ($C/C_0$) versus irradiation time, where $C_0$ and $C$ are the initial concentration and concentration at reaction time $t$, respectively. The degradation of MO is negligible in the absence of a photocatalyst. Both Ag$_2$Mo$_2$O$_7$ and AgI show poor photocatalytic performance, i.e., only 7.6% and 3.3% of MO can be degraded within 90 min, respectively. AgI/Ag$_2$Mo$_2$O$_7$ composites exhibit superior photocatalytic activities, and the degradation efficiencies of MO increase gradually with the growing AgI content. Among these composite photocatalysts, S5 exhibits the highest degradation efficiency of 80% after 90 min irradiation. S5 also displays a higher photocatalytic activity in the degradation of MO than the optimal photocatalyst of Ag/AgCl/Ag$_2$MoO$_4$ reported in our previous study.$^{28}$ (Figure S7). Figure 7b shows the time-
dependent UV−vis spectra of MO (10 mg/L) on S5. It can be seen that the absorption peak of MO decreases with the prolongation of irradiation time, and characteristic absorption peak at around 464 nm of MO almost disappear after irradiation for 90 min. The total organic carbon (TOC) analysis indicates that there is no decrease in the TOC value after reaction for 90 min (with respect to the TOC value of the fresh MO solution), indicating that MO is degraded, by using S4, into colorless organic products.

The corresponding pseudo-first-order rate constant (k) can be calculated by the following equation: \[ \ln(C_0/C) = kt \]
where \( C_0 \) and \( C \) are initial concentration and the concentration of MO after reaction for 90 min.
rhodamine B (RhB) at irradiation time $t$, respectively. As shown in Figure S8, the reaction in the first 15 min of reaction is much faster than the reaction afterward. In each stage, S5 is still the most active catalyst.

The stability of S5 was investigated by a four-run recycling experiments under the same condition, and the result is displayed in Figure 8a (containing the dark adsorption for 30 min). After four cycles, S5 still exhibits high activity for the degradation of MO, and the MO degradation efficiency is 77.6%, slightly dropping 2.5%, which may be attributed to the transformation of Ag$^+$ into Ag$^0$ during the photocatalytic process. The formation of Ag$^0$ has been confirmed via XRD and XPS. Compared to the fresh S5 (Figure 8b), the XRD pattern of the used S5 collected after the cycling runs shows a weak peak located at $2\theta = 38.1^\circ$, corresponding to the (111) facets of cubic Ag$^0$ (JCPDS No. 040783). The XPS spectrum also shows two peaks of Ag$^0$ located at 368.1 and 374.1 eV in S5 after four cycling runs (Figure 8b,c). The result is in accordance with the SEM−EDS result showing the higher content of Ag after reaction (Figure S9).

As for the photodegradation of RhB, the results presented in Figure 9 depict a trend similar to the trend seen in the degradation of MO, except that AgI is more active than Ag$_2$Mo$_2$O$_7$ in this reaction. As seen in Figure 9a, the dye molecules’ capacity to adsorb S1−S5 composites in the dark is enhanced in turn due to the increased $S_{BET}$. From the degradation curves of RhB (Figure 9b), it can be observed that an obvious blue shift occurs with the decrease in the maximum absorption peak. The phenomenon of the blue shift implies the de-ethylation of RhB during its degradation process.$^{60}$ The kinetics of the photocatalytic degradation of RhB are also fit by the pseudo-first-order kinetics linear function model (Figure S10). S5 shows the highest photocatalytic degradation rate ($5.06 \times 10^{-2}$ min$^{-1}$), greatly higher than that of Ag$_2$Mo$_2$O$_7$ ($5.63 \times 10^{-5}$ min$^{-1}$) and AgI ($7.25 \times 10^{-3}$ min$^{-1}$).

The TOC value of the solution collected at 90 min irradiation (by using S5 as a catalyst) divided by the TOC value of the fresh RhB solution is 59.6%, i.e., the TOC value decreases by 40.4%. The decrease percentage is similar to the decrease in $C_0/C$ value caused by dark adsorption (Figure 9a), implying that RhB is degraded into colorless organic products using this catalyst upon light irradiation.

In addition, colorless organic compound of tetracycline hydrochloride (TC, 20 mg/L) and levofloxacin (LEV, 20 mg/L) were also used to assess the photocatalytic activity of the samples (Figure 10). Both AgI and Ag$_2$Mo$_2$O$_7$ show poor removal efficiency in TC and LEV degradation. The degradation efficiencies of TC and LEV are improved significantly after coupling Ag$_2$Mo$_2$O$_7$ with different amounts of AgI, and S5 presents the highest degradation efficiencies of 64.3% (TC) and 64.5% (LEV), respectively. Therefore, this result can confirm the prominent photocatalytic performance of S5.

2.3. Photocatalytic Reaction Mechanism. Photoluminescence (PL) emission was employed to investigate the migration, separation, and recombination of photoinduced charge carriers. A lower PL emission peak intensity indicates a higher separation efficiency of the photoexcited electron−hole pairs.$^{29,61}$ As seen from the PL spectra of Ag$_2$Mo$_2$O$_7$, AgI, and S5 in Figure 11a, both Ag$_2$Mo$_2$O$_7$ and AgI exhibit higher PL intensity, which implies the possibility of a faster recombination of charge carriers. On the contrary, S5 displays lower PL signals, suggesting that the recombination of the electrons and holes is effectively restrained and the electron-transfer rate is greatly facilitated.

To get further insight into the charge-transfer process of the samples, electrochemical impedance spectroscopy (EIS) were
recorded. As illustrated in Figure 11b, the arc radius on the EIS Nyquist plot of SS is considerably smaller than that of Ag₂Mo₂O₇ and AgI, validating that SS possesses a weaker charge-transfer resistance and a higher photocatalytic activity, consistent with the result of PL.

Radical-trapping experiments were implemented on MO decomposition of SS via adding scavengers to capture the active species generated during photocatalysis. Herein, p-benzoquinone (BQ, 0.02 mmol), ethylenediaminetetra-acetic acid disodium salt (EDTA-2Na, 1 mmol), and isopropyl alcohol (IPA, 1 mmol) were used as scavengers for superoxide anion radicals (•O₂⁻), photogenerated holes (h⁺), and hydroxyl radicals (•OH), respectively. As shown in Figure 12, the MO degradation is significantly inhibited after the addition of BQ, with the efficiency decreased from 80.0% (no scavenger) to 29.4% (in the presence of BQ), indicating that •O₂⁻ is the predominant active species in the photocatalytic degradation process. When EDTA-2Na is introduced to the reaction system, the MO degradation efficiency drops from 80.0% (no scavenger) to 50.1% (in the presence of EDTA-2Na), suggesting that h⁺ plays a secondary role. In regard to •OH, the degradation of MO is slightly suppressed after the addition of IPA. Thus, hydroxyl radicals (•OH) are not actively involved in the photocatalytic process. To summarize, •O₂⁻ and h⁺ are the mainly active species in the photocatalysis.

The radical-capture experiments were also conducted on LEV decomposition using SS. As shown in Figure S11, the degradation of LEV is greatly restrained after the addition of EDTA-2Na and slightly hindered in the presence of IPA, suggesting the key role of h⁺ in the degradation process. The experiment using BQ does not generate conclusive results due to the interference of the characteristic absorption peak of LEV. This is also the case with TC (data not shown).

The existence of active species was further confirmed by electron spin resonance (ESR) spin-trap techniques utilizing S₅, 5,5-dimethyl-1-pyrroline-N-oxide (DMPO, a spin-trapping reagent). Remarkably, there are no signals in the dark, whereas intensive characteristic signals can be detected under visible-light irradiation. As shown in Figure 13a, four strong characteristic peaks with intensities of 1:2:2:1 appear in the aqueous dispersions of SS under visible-light irradiation, as attributed to the DMPO--•OH spin adducts, and the peak intensity is significantly stronger than those of Ag₂Mo₂O₇ and AgI. Meanwhile, six characteristic peaks of DMPO--•O₂⁻ are also distinctly observed under visible-light illumination (Figure 13b), and SS shows the strongest peak intensity among the three samples, in agreement with the enhanced photocatalytic performance of SS. Overall, the ESR results demonstrate that •O₂⁻ and •OH are generated during the photocatalytic degradation process using SS. However, it should be mentioned that •OH is not relevant to photocatalytic degradation in this study according to the radical-capture experiments (Figure 12) although it is indeed generated (Figure 13a).

Two photocatalytic mechanisms are proposed and illustrated in Figure 14. Both Ag₂Mo₂O₇ and AgI can respond to visible light, and photoinduced electrons can be excited to the conduction band (CB). Since the CB edge of Ag₂Mo₂O₇ (0.24 V) is more positive than that of AgI (-0.42 V), the excited electrons (e⁻) will migrate from the CB of AgI to the CB of Ag₂Mo₂O₇, whereas the photogenerated holes (h⁺) left behind will transfer from the VB of Ag₂Mo₂O₇ to the VB of AgI (Figure 14a). However, due to the much more positive edge potential of Ag₂Mo₂O₇ (0.24 V) than the potential of O₂/•O₂⁻ (-0.33 V), the electrons accumulated in the CB of Ag₂Mo₂O₇ are unable to transform O₂ to •O₂⁻. Similarly, the transformed holes also do not work in the system, owing to the lower oxidation potential of AgI (2.39 V) than that of H₂O/•OH (2.72 V). Thus, a Z-scheme mechanism may be more reasonable. As shown in Figure 14b, the excited electrons in the CB of Ag₂Mo₂O₇ combine with the holes in the VB of AgI. Therefore, the preserved photoinduced electrons in the
CB of AgI with high reduction ability will reduce oxygen to produce $\text{O}_2^-$, and the maintained photogenerated holes in the VB of Ag$_2$Mo$_2$O$_7$ with high oxidation ability can directly react with pollutants to produce the degradation products. In general, the efficient Z-scheme heterojunction can optimize the redox ability of photocatalysts and lead to superior photocatalytic performance.67

3. CONCLUSIONS

Rodlike AgI/Ag$_2$Mo$_2$O$_7$ composites with different molar ratios were fabricated via reacting Ag$_2$Mo$_2$O$_7$ microrods with an aqueous KI solution. The characterization results showed that AgI nanoparticles are evenly distributed on the surface of Ag$_2$Mo$_2$O$_7$, and heterostructures are formed. Compared with pristine Ag$_2$Mo$_2$O$_7$ and AgI, the resultant AgI/Ag$_2$Mo$_2$O$_7$ heterojunctions displayed better photocatalytic performance for the degradation of organic pollutants under visible-light irradiation, and the optimized AgI/Ag$_2$Mo$_2$O$_7$ molar ratio was 4:1. Good recyclability was also obtained for the optimal AgI/Ag$_2$Mo$_2$O$_7$ sample (S5) in the process of photodegradation. Superoxide anion radicals ($\text{O}_2^-$) and photogenerated holes (h$^+$) were found to be the main active species in the photocatalysis. A Z-scheme photocatalytic mechanism was proposed.

4. EXPERIMENTAL SECTION

4.1. Materials. AgNO$_3$, Na$_2$MoO$_4$·2H$_2$O, KI, HNO$_3$, rhodamine B (RhB), and methyl orange (MO) of analytical grade were purchased from Sinopharm Chemical Reagent. Levofloxacin (LEV) and tetracycline hydrochloride (TC) of analytical grade were obtained from Aladdin. Deionized water was generated from Laboratory Water Purification System (Master-Q30, HHitech).

4.2. Preparation of Ag$_2$Mo$_2$O$_7$ Microrods. Ag$_2$Mo$_2$O$_7$ microrods were synthesized by a facile hydrothermal method.56 In a typical procedure, 1 mmol AgNO$_3$ was dissolved in 40 mL deionized water to form solution A and 0.5 mmol Na$_2$MoO$_4$·2H$_2$O was dissolved in 40 mL deionized water to form solution B. Then, solution A was added into solution B dropwise under magnetic stirring (700 rpm) at room temperature. Subsequently, the pH value of the mixture, monitored by a pH meter, was adjusted to 2 using HNO$_3$ solution (0.7 M), and the mixture was magnetically stirred for 30 min in the dark. The resulting mixture was transferred into a Teflon-lined stainless autoclave of 100 mL capacity, heated to 150 °C for 12 h, and then cooled down to room temperature. The precipitate was separated by centrifugation and washed with deionized water. This centrifugation and washing process was repeated several times. Finally, the product was dried at 60 °C for 12 h.

4.3. Preparation of AgI/Ag$_2$Mo$_2$O$_7$ Composites. The obtained Ag$_2$Mo$_2$O$_7$ powders (0.26 g) were dispersed in 100 mL deionized water and treated in an ultrasonic bath for 30 min to allow for the dispersion of Ag$_2$Mo$_2$O$_7$ powders in water. Then, a certain amount (0.11, 0.20, 0.33, 0.50, or 0.67 mmol) of KI was dissolved in 40 mL deionized water, and the KI solution was added dropwise under vigorous stirring (700 rpm). The suspension turned yellow and was kept stirring for 1 h at room temperature. Subsequently, the obtained samples were washed with distilled water several times and then dried at 60 °C for 12 h. The final AgI/Ag$_2$Mo$_2$O$_7$ composites with different theoretical AgI/Ag$_2$Mo$_2$O$_7$ molar ratios of 1:4, 1:2, 1:1, 2:1, and 4:1 are denoted as S1, S2, S3, S4, and S5, respectively. For comparison, pristine AgI was prepared by precipitation using 2 mmol AgNO$_3$ and 2 mmol KI.

4.4. Characterization. X-ray diffraction (XRD) experiments for determining the crystal phases were performed using an X’Pert PRO MPD X-ray diffractometer (Rigaku, Japan) using Cu Kα radiation at 40 kV and 30 mA. The scanning speed was chosen to be 10° min$^{-1}$. X-ray photoelectron spectroscopy (XPS) measurements for analyzing the oxidation states of elements were carried out on an ESCALAB 250XI photoelectron spectroscopy instrument (Thermo Fisher). Scanning electron microscope (SEM) experiments for characterizing the sample on an electrochemical analyzer (CHI 1030B, Chenhua Instrument Company). Electron spin resonance (ESR) data were acquired by a Bruker A300 spectrometer (Bremen, Germany). Optical diffuse-reflectance UV–vis spectra were recorded on a U-3900H spectrophotometer (Hitachi, Japan). Photoluminescence (PL) spectra were obtained using an FLS1000 Evolution instrument at an excitation wavelength of 355 nm (Edinburgh, England). Electrochemical impedance spectroscopy (EIS) was used to characterize the sample on an electrochemical analyzer (CHI 1030B, Chenhua Instrument Company). Electron spin resonance (ESR) data were acquired by a Bruker A300 spectrometer. The signals of radicals $^\bullet\text{OH}$ and $^\bullet\text{O}_2^-$ were spin-trapped by 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) dissolved in H$_2$O and absolute methanol, respectively.28

4.5. Photocatalytic Activity. Photocatalytic degradation of rhodamine B (RhB, 10 mg/L), methyl orange (MO, 10 mg/L), levofloxacin (LEV, 20 mg/L), and tetracycline hydrochloride (TC, 20 mg/L) was carried out under visible light generated by an Xe lamp (300 W, HSX-F300, Beijing NBeT). Figure 14. Schematic illustration of two different mechanisms over AgI/Ag$_2$Mo$_2$O$_7$: (a) conventional heterojunction and (b) Z-scheme heterojunction systems.

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Technology Co., Ltd.) coupled with a UV-cutoff filter (λ > 420 nm), as shown in Figure S1.28 Briefly, 30 mg photocatalysts were dispersed in 50 mL contaminant solution (RHb, MO, LEV, or TC solution) in a 100 mL beaker, and the distance between the solution surface and the Xe lamp was 30 cm (Figure S1).

The suspension was stirred vigorously (700 rpm) in the dark for 30 min to reach the adsorption–desorption equilibrium. After that, visible-light irradiation was conducted. At given irradiation time intervals, 3.5 mL of the suspension (containing the suspension and fine catalyst powders dispersed within) was sampled and then centrifuged at a speed of 12 000 rpm for 20 min to separate the catalyst powders and solution. The obtained supernatant (solution) was analyzed by a UV-2000PC spectrometer by checking its characteristic absorbance at maximum absorption wavelength. The TOC values of the liquid phases were determined by a TOC analyzer (Shimadzu TOC-VCPC).

For reusability test, the used catalyst powders obtained after one photocatalytic cycle were collected and washed with distilled water, dried at 60 °C, and then reused. Due to the unavoidable loss of catalyst powders during the sampling and recovery processes, parallel photocatalytic runs were conducted to replenish the spent catalysts.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b00806.

Characterization data and reaction testing data of relevant samples, XRD patterns, XPS spectra, SEM images, SEM photo and EDS pattern of S5, nitrogen adsorption–desorption isotherms, UV–vis diffuse reflectance spectra of S1–S5 (PDF)

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Notes

The authors declare no competing financial interest.

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