1 Introduction

Nowadays, photocatalysis technology is regarded as one of the best ways to alleviate energy and environmental issues. TiO₂ is a widely known photocatalyst for water splitting and decomposing organic pollutants. However, TiO₂ is only sensitive to UV radiation due to its large bandgap (3.2 eV). Accordingly, a maximum of 6% of solar energy can be harvested using this material, which limits its practical application. This obvious disadvantage is the main motivation for the search for new and more efficient visible-light-driven photocatalysts.

Among the developed photocatalysts, monoclinic structured BiVO₄ has emerged as a potentially suitable visible-light-driven photocatalyst because of its exceptional properties, such as narrow bandgap, good photocatalytic activity, and nontoxicity. However, the practical applications of BiVO₄ is significantly limited owing to the weak charge-transfer rate and rapid recombination of photoinduced charge carriers.²,³ It has been reported that constructing semiconductor heterojunction structures could promote the photoexcited charge carrier separation, and hence improve the performance of photocatalyst. Cao et al. prepared Au/BiVO₄ nanocomposites with excellent activity for water splitting owing to the improved charge separation and surface plasmon resonance of Au nanoparticles.⁴ Regmi et al. reported that Ag-modified BiVO₄ sample exhibits better photocatalytic activity than BiVO₄, which can effectively degrade bisphenol A and deactivate the Escherichia coli.⁵ Li et al. synthesized Ag₃PO₄/BiVO₄ composites with type-II heterojunction, which can effectively degrade methylene blue (MB).⁶ Li et al. reported that the MoS₂/BiVO₄ composites also show excellent photoactivity for decoloring MB.⁷ Similarly, a number of studies of BiVO₄ coupled with metal nanoparticles or other oxides were reported for the purpose of improving photocatalytic activity as well, such as Bi/BiVO₄,⁸ Pd/BiVO₄,⁹ CdS/BiVO₄,¹⁰ g-C₃N₄/BiVO₄,¹¹ Bi₂S₃/BiVO₄,¹² Bi₂O₃/BiVO₄,¹³ WO₃/BiVO₄,¹⁴ Ag₃PO₄/BiVO₄,¹⁵ Cu₃O/BiVO₄,¹⁶ and BiVO₄/RGO.¹⁷ Ag₃S has aroused much research interest owing to its narrow bandgap, which means that it can utilize more energy from the solar light spectrum. Therefore, Ag₃S can act as photocatalyst or suitable sensitizer for photocatalysts under visible light irradiation. For example, Ghafoor et al. reported that Ag₃S nanoparticles photosensitized TiO₂ nanofibers display enhanced simulated solar light driven photocatalytic performance.¹⁸ Kumar et al. reported that a p–n heterojunction was fabricated by modifying NaNbO₃ nanorods with Ag₃S particle, which possesses excellent photoelectrochemical and photocatalytic activity.¹⁹ Jiang et al. found that compared with g-C₃N₄, the Ag₂S/g-C₃N₄ photocatalyst exhibits improved activity for H₂ evolution. Interessingly, Ag was formed in the process of H₂ production. It was suggested that both Ag and Ag₂S played a synergistic role in hydrogen production.²⁰ Guan et al. prepared a p–n junction of Ag₃S/BiVO₄ with significantly improved
photoelectrochemical water splitting ability.\textsuperscript{21} Zhao et al. reported that Ag\textsubscript{2}S/BiVO\textsubscript{4} junction displays a better photocatalytic efficiency with the aid of plasmon resonance of Ag nanoparticles.\textsuperscript{22}

However, it is known that the redox ability of photoexcited electrons and holes on reaction sites deteriorated during the charge transfer process in p–n or type-II heterojunction. As a result, the traditional semiconductor heterojunction could not exhibit both excellent charge-separation efficiency and powerful redox ability simultaneously.\textsuperscript{23} To overcome this drawback, the Z-scheme photocatalytic system has been developed. It was believed that the Z-scheme photocatalytic system not only promotes the separation of the photo-induced carriers, but also can optimize carriers redox ability.\textsuperscript{24–28} For example, Tada et al. reported a Z-scheme CdS–Au–TiO\textsubscript{2} composites with high photocatalytic activity, which exhibit an electron migration of TiO\textsubscript{2} \rightarrow Au \rightarrow CdS.\textsuperscript{27} This unique electron migration is different with previously reported CdS/TiO\textsubscript{2},\textsuperscript{28} which was attributed to the Au nanoparticles acting as the electron mediator. Yin et al. reported that C\textsubscript{3}N\textsubscript{4}/Cu\textsubscript{2}O photocatalyst with a p–n heterojunction can be changed to a Z-scheme system C\textsubscript{3}N\textsubscript{4}/Pd/Cu\textsubscript{2}O by inserting metal Pd into the C\textsubscript{3}N\textsubscript{4}/Cu\textsubscript{2}O interface, which has enhanced photocatalytic activity and stability.\textsuperscript{29} The inserted Pd nanocubes in the stack structure and the unique design are the critical roles in the formation of Z-scheme system. Deng et al. also synthesized a Z-scheme system BiVO\textsubscript{4}/Ag/CuO by depositing metallic Ag to the p–n heterojunction BiVO\textsubscript{4}/CuO.\textsuperscript{30} Lin et al. reported that a Z-scheme electron migration was confirmed in Ag\textsubscript{3}PO\textsubscript{4}/Ag/Bl\textsubscript{2}M\textsubscript{O}O\textsubscript{6} composites, which is different with typical Ag\textsubscript{3}PO\textsubscript{4}/Bl\textsubscript{2}M\textsubscript{O}O\textsubscript{6} type-II heterojunction.\textsuperscript{31,32} Li et al. found that the Ag/Ag\textsubscript{3}PO\textsubscript{4}/W\textsubscript{O}O\textsubscript{3} nanocomposites show better photocatalytic performance than traditional Ag\textsubscript{3}PO\textsubscript{4}/WO\textsubscript{3} heterojunction, which can be attributed to the formation of Z-scheme structure.\textsuperscript{33} Zhao et al. prepared Z-scheme g-C\textsubscript{3}N\textsubscript{4}/Au/P25 composites with excellent photoactivity by introducing metal Au to the g-C\textsubscript{3}N\textsubscript{4}/P25 heterojunction.\textsuperscript{34} Liu et al. fabricated Z-scheme Cu\textsubscript{2}O/Au@CeO\textsubscript{2} composites with strong redox ability by embedding Au nanoparticles in the yolk–shell Cu\textsubscript{2}O@CeO\textsubscript{2} structure, which can effectively oxidize amines into imines.\textsuperscript{35} Bao et al. prepared efficient Z-scheme Cu\textsubscript{2}O/Cu/g-C\textsubscript{3}N\textsubscript{4} photocatalyst for decomposing phenol via reduction route, in which partial metal Cu was preserved as a bridge for the transfer of photoexcited charge.\textsuperscript{36} Shen et al. reported that when reduced graphene oxide was introduced to a Cu\textsubscript{2}O/Fe\textsubscript{2}O\textsubscript{3} type-II junction, the electron migration of Fe\textsubscript{2}O\textsubscript{3} \rightarrow RGO \rightarrow Cu\textsubscript{2}O was confirmed in the Z-scheme RGO-Cu\textsubscript{2}O/Fe\textsubscript{2}O\textsubscript{3} composites.\textsuperscript{37} Similarly, some Z-scheme photocatalysts were prepared by introducing Ag or Au to a type-II heterojunction, such as Ag\textsubscript{2}CO\textsubscript{3}/Ag/AgBr,\textsuperscript{38} g-C\textsubscript{3}N\textsubscript{4}/Ag/Ag\textsubscript{3}PO\textsubscript{4} and Au/TiO\textsubscript{2}/g-C\textsubscript{3}N\textsubscript{4}.\textsuperscript{39} Therefore, it was possible that a Z-scheme photocatalytic system could be fabricated by properly adding electron mediator to a p–n or type-II heterojunction.

Herein, the Z-scheme system BiVO\textsubscript{4}/Ag/Ag\textsubscript{2}S photocatalyst was prepared via two-step route in this work. The photocatalytic activity of the synthesized Z-scheme BiVO\textsubscript{4}/Ag/Ag\textsubscript{2}S photocatalyst was investigated in this study. Additionally, the possible mechanism of the improved photocatalytic performance of BiVO\textsubscript{4}/Ag/Ag\textsubscript{2}S was discussed.

## 2 Experimental

### 2.1 Synthesis of photocatalysts

The BiVO\textsubscript{4} sample was obtained via a previously reported route.\textsuperscript{40} 0.3 g BiVO\textsubscript{4} and 0.1 mmol AgNO\textsubscript{3} were added into 50 mL of distilled (DI) water and stirred for 3 h. Then, the mixture was added with 5 mL of methanol and irradiated by a UV light (100 W) for 1 h. The resulting powders (BiVO\textsubscript{4}/Ag composites) were collected by centrifuge and washed with DI water and ethanol, then dried at 70 °C for 8 h. 0.3 g as-synthesized BiVO\textsubscript{4}/Ag composites was ultrasonically dispersed in 50 mL DI water. Then, AgNO\textsubscript{3} was added and stirred for 1 h. Subsequently, 50 mL of Na\textsubscript{2}S solution was dropped into the mixture and stirred for 8 h under dark condition. Similarly, the obtained product was centrifuged, washed and dried, in which the weight ratio of BiVO\textsubscript{4}, Ag and Ag\textsubscript{2}S is 100 : 1 : 1.

### 2.2 Characterization of the as-prepared samples

X-ray diffraction (XRD) was recorded by X-ray diffractometer (Bruker D8) with Cu Kz radiation. The samples’ morphologies were characterized by field emission scanning electron microscopy (JSM 6701F) and high-resolution transmission electron microscopy (HRTEM, FEI Tecnai G2 F20 S-TWIN). X-ray photoelectron spectroscopy (XPS) was collected on ESCALAB 250Xi to identify the chemical compositions and the chemical states of the sample. UV-vis diffuse reflectance spectra (DRS) of the samples were acquired using BaSO\textsubscript{4} as a reference material with a PerkinElmer Lambda 950 UV-vis spectrophotometer. Steady-state and time-resolved photoluminescence spectra (PL) were performed on FLS 920 fluorescence spectrometer.

### 2.3 Photoelectrochemical measurements

The photocurrent responses of as-synthesized photocatalysts were investigated on a Zahner PP211 electrochemical workstation in a three-electrode cell. The FTO coated with photocatalysts served as the working electrode. A Pt wire and an Ag/AgCl (saturated KCl) electrode were applied as counter and reference electrode, respectively. The photocurrent measurements were carried out in 0.1 M Na\textsubscript{2}SO\textsubscript{4} solution. A 30 W LED lamp with lighting wavelength of 420 nm was utilized as the light source. The light spectrum of the LED lamp is presented in Fig. S1.\textsuperscript{†}

### 2.4 Photocatalytic test

The photocatalytic activity of the samples was evaluated by photo-decomposing RhB. The obtained photocatalysts (50 mg) were dispersed into 50 mL RhB aqueous solution (10 mg L\textsuperscript{–1}) and stirred in a dark condition for 30 min to ensure an adsorption–desorption equilibrium before irradiation. A LED lamp (30 W, 420 nm) was used as the visible light source. During the photodegradation experiment, the suspension was under continuous magnetic stirring. 5 mL of reaction solution was taken at 30 min intervals for analysis. The RhB concentration

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\textsuperscript{†} This paper is an RSC Advances Paper.
was monitored by Lambda 950 spectroscopy at a wavelength of 553 nm.

2.5 Computational details

Energy band structures and DOS of BiVO$_4$ and Ag$_2$S were investigated by the DFT method, in which plane-wave pseudopotential with CASTEP code was adopted. The generalized gradient approximation with the Perdew–Burke–Ernzerhof was applied as the exchange and correlation terms. The cutoff energies of 450 eV were used for all calculations. Monkhorst-Pack K-points grids of 5 $\times$ 5 $\times$ 2 and 6 $\times$ 3 $\times$ 3 were applied for BiVO$_4$ and Ag$_2$S, respectively.

3 Results and discussion

Fig. 1 presents the XRD patterns of the as-synthesized BiVO$_4$, Ag$_2$S, BiVO$_4$/Ag and BiVO$_4$/Ag/Ag$_2$S samples. For the BiVO$_4$ and Ag$_2$S samples, all the peaks could be assigned to BiVO$_4$ (JCPDS 14-0668) and Ag$_2$S (JCPDS 14-0072) respectively. The XRD patterns of BiVO$_4$, BiVO$_4$/Ag and BiVO$_4$/Ag/Ag$_2$S samples were similar. No diffraction peaks from Ag are observed in the BiVO$_4$/Ag sample. Similar phenomenon was observed in the XRD pattern of BiVO$_4$/Ag/Ag$_2$S sample and Ag$_2$S was not detected as Ag sample. Similar phenomenon was observed in the XRD patterns of the as-obtained Ag$_2$S, BiVO$_4$, BiVO$_4$/Ag and BiVO$_4$/Ag/Ag$_2$S samples. For the BiVO$_4$ and Ag$_2$S samples, all the peaks could be assigned to BiVO$_4$ (JCPDS 14-0668) and Ag$_2$S (JCPDS 14-0072) respectively. The XRD patterns of BiVO$_4$/Ag/Ag$_2$S samples were indexed to Ag (111) and Ag$_2$S (110), respectively. This result indicates that some Ag$_2$S nanoparticles were formed on the Ag particles.

X-ray photoelectron spectroscopy (XPS) provided further evidence as to the existence of Ag and Ag$_2$S in the ternary BiVO$_4$/Ag/Ag$_2$S composites. Ag, S, Bi, V and O elements were detected by the XPS survey spectrum of the ternary composites, as presented in Fig. 3a. From high resolution XPS analysis as depicted in Fig. 3b, two strong peaks at 373.5 and 374.2 eV were observed, which are indexed to Ag 3d$_{3/2}$ and Ag 3d$_{5/2}$, respectively. These two peaks could be fitted by four bands. Two peaks at 368.5 and 374.5 eV correspond to Ag$^0$ 3d$_{3/2}$ and 3d$_{5/2}$ respectively, which demonstrated the presence of metal Ag. Another two peaks at 368.0 and 374.0 eV correspond to Ag$^+$ 3d$_{3/2}$ and 3d$_{5/2}$, respectively. Furthermore, the peak located at 160.8 eV can be assigned to S 2p binding energy for Ag$_2$S. Fig. 3c. It demonstrates that both Ag and Ag$_2$S were contained in the as-prepared BiVO$_4$/Ag/Ag$_2$S sample. The Fig. 3d exhibits two peaks at 159.2 and 164.3 eV, which are ascribed to Bi 4f$^{7/2}$ and Bi 4f$^{5/2}$ of Bi$^{3+}$ in the BiVO$_4$, respectively. Two peaks at 516.9 and 524.3 eV (Fig. 3e) are attributed to V 2p$^{5/2}$ and V 2p$^{3/2}$ of V$^{5+}$ in the BiVO$_4$, respectively. Fig. 3f, the O 1s binding energy was observed at about 529.9 eV. The other O 1s peak can be attributed to –OH group or chemisorbed water molecule on BiVO$_4$/Ag/Ag$_2$S composites surface. Basing on the XPS result, the SEM and HRTEM images, it was suggested that the ternary BiVO$_4$/Ag/Ag$_2$S photocatalyst was successfully fabricated.

Fig. 4a depicts the optical property of the as-prepared samples. It can be found that all BiVO$_4$ based samples showed a strong absorption band in the 420–530 nm wavelength range, which suggested that they can absorb considerable amounts of visible light in this range. Therefore, the as-prepared BiVO$_4$ based samples could act as visible-light-driven photocatalysts. Additionally, the bandgap of photocatalyst can be calculated by the following equation: 46

\[
(\alpha h\nu)^{\alpha} = A(h\nu - E_g)
\]

where $\alpha$, $h$, $\nu$, $E_g$, and $A$ are the absorption coefficient, Planck’s constant, the light frequency, the bandgap, and a constant, respectively. $n = 1/2$ is for an indirect transmission; $n = 2$ is for a direct transmission. By plotting $(\alpha h\nu)^{1/2}$ vs. $h\nu$ (Fig. 4b), the bandgaps of the BiVO$_4$, BiVO$_4$/Ag, BiVO$_4$/Ag$_2$S and BiVO$_4$/Ag/Ag$_2$S photocatalysts are evaluated to be 2.40, 2.36, 2.34 and 2.35 eV, respectively. It suggests that the bandgap width of BiVO$_4$ was slightly decreased by co-depositing Ag and Ag$_2$S nanoparticles.

Fig. 5a displays the PL spectra of BiVO$_4$, BiVO$_4$/Ag, BiVO$_4$/Ag$_2$S and BiVO$_4$/Ag/Ag$_2$S samples. It is widely accepted that high PL intensity suggests rapid recombination of excited pairs, and results in poor photocatalytic activity. The PL peak located at about 545 nm was recorded for all samples, which was result
from the photogenerated carrier recombination in BiVO₄ particles. Compared with BiVO₄, both the BiVO₄/Ag and BiVO₄/Ag₂S display lower PL intensity, indicating that the recombination of carriers could be suppressed by modifying with Ag or Ag₂S nanoparticles. The ternary BiVO₄/Ag/Ag₂S sample shows the lowest PL intensity, which implying that it has the lowest carrier recombination rate. This is also confirmed by the time-resolved PL spectra (Fig. S2 and Table S1†). It is suggested that the synergistic effect of the Ag and Ag₂S nanoparticles play a key role to promote the separation of photoexcited carriers in the BiVO₄/Ag/Ag₂S composites.

To further understand the separation and migration efficiency of photoinduced electron–hole pairs, the photocurrent responses under dark and LED light irradiation were measured. As shown in Fig. 5b, the photocurrents of the prepared samples were stable and reversible at light-on and light-off. It is well known that larger photocurrent indicated a higher separation efficiency of photoexcited carriers. In comparison with BiVO₄, BiVO₄/Ag and BiVO₄/Ag₂S, BiVO₄/Ag/Ag₂S composites exhibited the highest photocurrent response density, about 4.5, 2.2 and 1.5 times that of BiVO₄, BiVO₄/Ag and BiVO₄/Ag₂S, respectively. It indicates that the BiVO₄/Ag/Ag₂S composites exhibit efficient
charge separation, which is in agreement with the PL spectroscopy results.

Fig. 6a depicts the photoactivity of the as-synthesized catalysts, which was estimated by degrading RhB. When the pure BiVO$_4$ sample was used as photocatalyst, only about 5% of RhB was degraded after 120 min irradiation. For the binary catalysts of BiVO$_4$/Ag and BiVO$_4$/Ag$_2$S, about 39% and 42% of RhB were degraded, respectively. It indicates that the photocatalytic activity of BiVO$_4$ could be simply enhanced by decorating with Ag or Ag$_2$S nanoparticles. The BiVO$_4$/Ag/Ag$_2$S photocatalyst shows excellent photocatalytic performance compared with other as-prepared samples. About 69% of RhB were degraded by the ternary composites. To directly show the improved photocatalytic activity of BiVO$_4$/Ag/Ag$_2$S sample, the degradation
kinetics for the removal of RhB were calculated by the pseudo-first-order reaction:

$$\ln \frac{C}{C_0} = -k \times t$$

where $C_0$ and $C$ are the concentration of RhB solution after adsorption and at the irradiation time $t$, respectively, $k$ is the apparent reaction rate constant. As illustrated in Fig. 6b, the rate constants corresponding to BiVO$_4$, BiVO$_4$/Ag, BiVO$_4$/Ag$_2$S,
and BiVO₄/Ag/Ag₂S samples were estimated to be 0.0003, 0.0041, 0.0054 and 0.0095 min⁻¹, respectively. The BiVO₄/Ag/Ag₂S composites show the highest k value, which is about 1.76, 2.32, 31.7 times higher than that of BiVO₄/Ag₂S, BiVO₄/Ag and BiVO₄, respectively. Obviously, the BiVO₄/Ag/Ag₂S composites show enhanced photocatalytic efficiency, which can be attributed to the lower electron–hole pair recombination rate and higher photogenerated charge separation efficiency.

The stability of photocatalyst is a crucial issue in its practical application. Fig. 6c shows the recycled experiments of the photodegradation of RhB by using the BiVO₄/Ag/Ag₂S composites for five cycles (120 min LED light irradiation for each cycle). It can be seen that only slight deterioration of the BiVO₄/Ag/Ag₂S sample was observed after five cycles, which implies the good recyclability of the prepared photocatalyst.

As is known, the superoxide radical (‘O₂⁻’), holes (h⁺) and hydroxyl radical (‘OH) as active species play crucial roles in photocatalytic reaction. In order to evaluate the main active species, the trapping experiments were carried out. The reactive species can be removed by adding corresponding scavengers into reaction solutions. The function of different reactive species could be made clear based on the change of photocatalytic performance. In this study, p-benzoquinone (BQ), ammonium oxalate (AO) and isopropanol (IPA) were added to act as ‘O₂⁻’, h⁺ and ‘OH scavenger, respectively. As presented in Fig. 6d, the ability of the BiVO₄/Ag/Ag₂S sample to remove RhB was not affected by adding BQ, which suggesting that ‘O₂⁻’ radical does not participate in the photocatalytic reaction. However, when BQ and AO were added, the photocatalytic activity of the BiVO₄/Ag/Ag₂S composites decreased significantly. It demonstrates that h⁺ and ‘OH play important roles in the photocatalytic process.

To clarify the mechanism of the improved photocatalytic activity of the BiVO₄/Ag/Ag₂S composites, the band structure of the ternary system was studied. The band edge potentials of the valence band (VB) and conduction band (CB) of BiVO₄ and Ag₂S can be estimated according the following equations:

\[ E_{VB} = \chi - E^s + 0.5E_g \]
\[ E_{CB} = E_{VB} - E_g \]

where \( E_{VB} \) and \( E_{CB} \) are the VB and CB edge potential, respectively; \( \chi \) and \( E_g \) are the absolute electronegativity and bandgap energy of the semiconductor, respectively; \( E^s \) is fixed at 4.5 V. The \( E_g \) of Ag₂S is calculated to be 1.46 eV, as shown in Fig. S3, which is consist with previous report. Thus, the \( E_{VB} \) and \( E_{CB} \) of

![Fig. 7 Electronic band structures of (a) BiVO₄ and (b) Ag₂S and density of states of (c) BiVO₄ and (d) Ag₂S.](image-url)
Ag$_2$S are estimated as 1.20 and $-0.26$ V, versus the normal hydrogen electrode (NHE), respectively. Similarly, the $E_{\text{VB}}$ and $E_{\text{CB}}$ of BiVO$_4$ are 2.795 and 0.285 V, versus the NHE, respectively.

Fig. 7 presents the band structures and DOS of BiVO$_4$ and Ag$_2$S. The valence band maximum (VBM) and conduction band minimum (CBM) are located at Z and P point, respectively (Fig. 7a), which imply that BiVO$_4$ is an indirect bandgap semiconductor. Ag$_2$S belongs to the direct bandgap semiconductor because the position of VBM is same as that of CBM, as demonstrated in Fig. 7b. The bandgaps of BiVO$_4$ and Ag$_2$S are calculated to be 2.16 eV and 0.97 eV, respectively. However, these calculated bandgaps are smaller than experimental values (2.40 eV for BiVO$_4$ and 1.46 eV for Ag$_2$S), which are resulted from the well-known drawback of DFT calculations.

As shown in Fig. 7c, the upper VB of BiVO$_4$ consists largely of O 2p, V 3d and a small amount of Bi 6s and Bi 6p states. Meanwhile, the CB of BiVO$_4$ mainly consist of O 2p, V 3d and Bi 6p states. For Ag$_2$S (Fig. 7d), the upper VB is mainly composed by Ag 4d states and a few of S 3p states, and the CB is mainly occupied by Ag 4p, Ag 5s and S 3p states. It is reasonable that the S 3p states result in the narrow bandgap of Ag$_2$S.

Based on the above results and discussion, the mechanism of the photodecomposition of RhB with the BiVO$_4$/Ag/Ag$_2$S composites is proposed, as shown in Fig. 8. When the ternary BiVO$_4$/Ag/Ag$_2$S composites were irradiated by LED light (420 nm), electrons and holes were generated in the CB and VB of BiVO$_4$ and Ag$_2$S. It is important to notice that the VB potential of Ag$_2$S (1.195 V vs. NHE) is above the ’OH/OH” potential (2.27 V vs. NHE at pH = 7), which demonstrating that the holes photogenerated in the VB of Ag$_2$S cannot reacted with OH$^-$ to produce ’OH active species. Therefore, it is not supposed that the photoinduced holes transfer from BiVO$_4$ to Ag$_2$S according to the traditional p-n heterojunction. It is suggested that a Z-scheme electron migration emerges in the ternary photocatalyst. The photoexcited electrons in the CB of BiVO$_4$ transferred to Ag and then recombined with the photoinduced holes in the VB of Ag$_2$S, which resulting in a better charge separation. The $E_{\text{VB}}$ of BiVO$_4$ (3.37 V vs. NHE) is below the ’OH/OH” potential. Hence, the photoexcited holes in the VB of BiVO$_4$ could reacted with OH$^-$ to generate ’OH. Additionally, the holes of BiVO$_4$ can directly oxidized the RhB dye. Consequently, both h$^+$ and ’OH play crucial roles in decomposing RhB molecule, which is consist with the trapping experimental results.

Fig. 8 Schematic illustrating the proposed degradation mechanism of RhB over the ternary BiVO$_4$/Ag/Ag$_2$S composites.

4 Conclusions

The Z-scheme system BiVO$_4$/Ag/Ag$_2$S photocatalyst was successfully prepared via two-step method. The as-synthesized ternary BiVO$_4$/Ag/Ag$_2$S composites exhibit higher separation efficiency and reduction of carrier recombination rate, which result in enhanced photocatalytic efficiency for decomposing RhB under LED light irradiation. The photocatalytic mechanism over the ternary composites was investigated in detail. It is suggested that Z-scheme electron migration of BiVO$_4$ $\rightarrow$ Ag $\rightarrow$ Ag$_2$S exists in the ternary system.

Conflicts of interest

There are no conflicts to declare.

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