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Synergistic Effects of Ag Nanoparticles/ $\text{BiV}_{1-x}\text{Mo}_x\text{O}_4$ with Enhanced Photocatalytic Activity

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Abstract

In recent years, BiVO_4 has drawn much attention as a novel photocatalyst given its excellent ability to absorb visible light. This work reports the development of Ag-modified $\text{BiV}_{1-x}\text{Mo}_x\text{O}_4$ composites through a facile hydrothermal synthesis with the subsequent photoinduced reduction of Ag^+ at almost neutral pH conditions. Metallic Ag nanoparticles were deposited on the (040) facet of Mo-doped BiVO_4 powders. The crystal structure and morphology of the as-prepared samples were studied by XRD and SEM analyses. Moreover, the photocatalytic performance of BiVO_4 , Ag/ BiVO_4 , and Ag-modified $\text{BiV}_{1-x}\text{Mo}_x\text{O}_4$ were evaluated by the degradation of rhodamine B (RhB). The Ag/ $\text{BiV}_{0.9925}\text{Mo}_{0.0075}\text{O}_4$ composite exhibited the most efficient photocatalytic performance. The present work provides greater insight into the application of BiVO_4 in the field of photocatalysis.

Keywords: Hydrothermal synthesis, Photocatalytic, Metal doping, Ag/ $\text{BiV}_{1-x}\text{Mo}_x\text{O}_4$

Background

Given the increasing environmental pollution and energy crises, the development of efficient and promising solutions to reduce energy shortages and protect the environment is paramount [1, 2]. Photocatalyst-based semiconductors, such as Bi_2WO_6 [3, 4], BiPO_4 [5, 6], Ag_3PO_4 [7, 8], and BiVO_4 [9–13], have attracted much attention due to their applications in the degradation of organic pollutants or hydrogen production from water splitting. Nevertheless, most of the existing oxide photocatalysts have very low light-response efficiencies primarily because they only respond to ultraviolet light due to their narrow bandgaps [14–16]. Additionally, the photoinduced electrons can easily recombine with holes leading to a lower optical performance [17, 18].

Due to its visible photocatalytic activity, wide bandgap of 2.42 eV, high stability, and non-toxicity, bismuth vanadate (BiVO_4) is a promising n-type semiconductor

photocatalyst [19–21]. However, its resulting carrier transfer efficiency is relatively poor, leading to the recombination of photogenerated electrons and holes, which severely limits the photocatalytic performance of BiVO_4 . Various studies have assessed BiVO_4 modifications [20, 22–24], and substitution or metal doping on BiVO_4 has been shown as the most efficient method to change its carrier transport efficiency. Metal element doping introduces new defects or charges in the crystal lattice [25], influencing the motion of electrons and the creation of holes under light irradiation [26, 27]. Adjustments to the distribution status or changes in the band structures can lead to changes in the activity of semiconductors [28]. For example, Thalluri et al. [29] introduced hexavalent molybdenum (Mo) at an almost neutral pH to substitute V while preserving the atomic ratio of fBiVO_4 , leading to the formation of a good crystal structure and considerable photocatalytic activity for water oxidation. Mo has a higher valence than V and therefore strengthens the n-type characteristics of the material [30]. Additionally, the photocatalytic activity of BiVO_4 is highly dependent on its various crystal facets. Recent studies on the deposition of noble metals, such as Ag, Cu, and Au, on the different facets of BiVO_4 have

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demonstrated good photocatalytic activity [31–33]. Li et al. [34] produced an Ag/BiVO₄ composite through the hydrothermal synthesis and photoreduction of Ag deposited on the (040) crystal facets of BiVO₄, leading to an enhanced photoelectrochemical performance, as indicated by the fast separation of the electron–hole pairs.

In the present study, we build on the facile hydrothermal synthesis approach of Li et al. [29] to obtain BiV_{0.9925}Mo_{0.0075}O₄ in weakly alkaline conditions, coupled with photoreduction deposition of Ag nanoparticles on the (040) facets of the as-produced substrate materials. Ag/BiV_{0.9925}Mo_{0.0075}O₄ composite photocatalysts were successfully synthesized and showed enhanced photocatalytic degradation of rhodamine B (RhB) under xenon lamp irradiation ($\lambda > 420$ nm) compared to the non-composite Ag-deposited or Mo-doped BiVO₄ materials. Herein, we report the preparation, characterization, and photocatalytic activity of BiVO₄, Ag/BiVO₄, BiV_{1-x}Mo_xO₄, and Ag/BiV_{1-x}Mo_xO₄ composites.

Experimental

Synthesis of BiVO₄ and BiV_{1-x}Mo_xO₄ Powders

Bismuth nitrate pentahydrate (Bi(NO₃)₃·5H₂O, analytical grade), ammonium metavanadate (NH₄VO₃, analytical grade), ammonium carbonate, and ammonium molybdate ((NH₄)₂MoO₄) were obtained from Sigma–Aldrich and used as received, without any further purification. All other chemicals used in the experiments were also of analytical grade, and deionized water was used for the preparation of the solutions. In a typical process, 3.7 mmol of Bi(NO₃)₃·5H₂O, 3.7 mmol of NH₄VO₃, and 12 mmol of (NH₄)₂CO₃ were dissolved in 75 mL of 1 M HNO₃ and stirred for approximately 30 min at room temperature until a clear solution was obtained. The pH of the mixture was adjusted to pH 8 with NaOH (2 M). The mixture was transferred to a 150-mL Teflon-lined stainless autoclave and heated for 12 h at 180 °C under autogenous pressure in an oven. The precipitate was filtered and washed three times with distilled water followed by ethanol and dried for 12 h at 60 °C in a drying oven.

The doped samples were prepared by replacing the equivalent weight of NH₄VO₃ with different amounts of Mo. Mo precursors were introduced such that a nominal 0.5, 0.75, and 1% atomic substitution of V was achieved.

Preparation of Ag/BiVO₄ and Ag/BiV_{1-x}Mo_xO₄ Samples

BiVO₄ (0.50 g) and AgNO₃ (0.05 g) were added to a (NH₄)₂C₂O₄ (0.8 g L⁻¹, 100 mL) aqueous solution in a 250-mL beaker in an ultrasonic bath until an evenly dispersed solution was formed. The resulting yellow mixture was then irradiated with a Xenon lamp for 30 min under magnetic stirring. The color of the system

turned from a vivid yellow to grayish-green, indicating the generation of metallic Ag in the reaction system. The resulting samples were then filtered, washed with DI water, and dried at 60 °C for 12 h to obtain the Ag/BiVO₄ and Ag/BiV_{1-x}Mo_xO₄ composites.

Photocatalytic Activity

Assessment of the photocatalytic activity was performed using the degradation rate of RhB. The experimental system for photodegradation was calibrated at a UV cut-off wavelength below 420 nm, and the irradiation height of the Xenon lamp was close to the height of the 250-mL beaker. In a typical procedure, the as-prepared photocatalyst (0.1 g) was well dispersed in a RhB aqueous solution (150 mL, 10 mg L⁻¹) under ultrasonication in a glass reactor equipped with a cooling water circulator to maintain a reaction system temperature of room temperature. The suspension was stirred for 30 min in the dark to reach the adsorption–desorption equilibrium and was then irradiated for 2 h with a Xenon lamp (300 W) under continuous stirring. A 5-mL aliquot of the suspension was taken every 30 min and centrifuged. The absorption spectrum of the obtained liquid

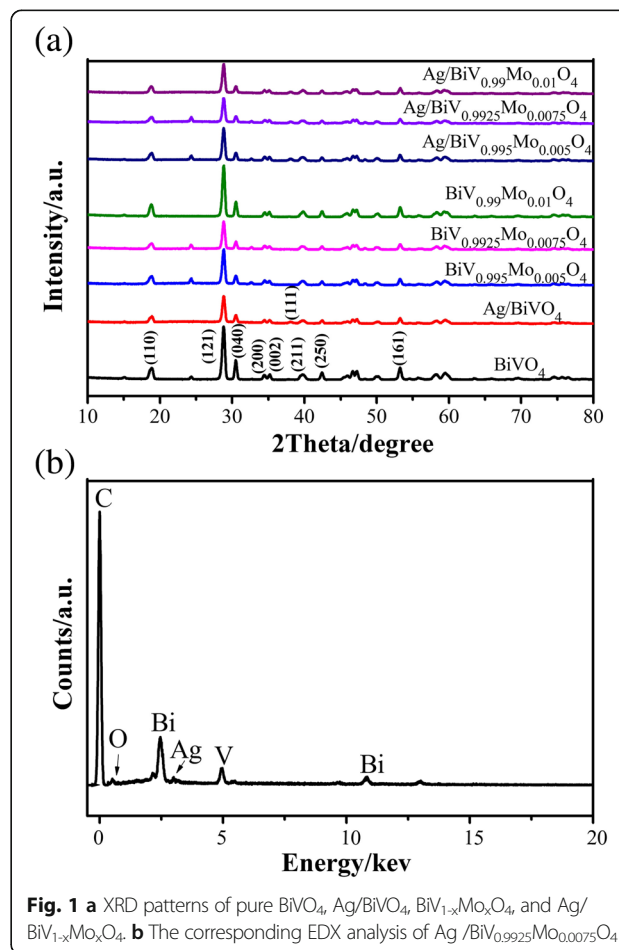


Fig. 1 a XRD patterns of pure BiVO₄, Ag/BiVO₄, BiV_{1-x}Mo_xO₄, and Ag/BiV_{1-x}Mo_xO₄. b The corresponding EDX analysis of Ag/BiV_{0.9925}Mo_{0.0075}O₄

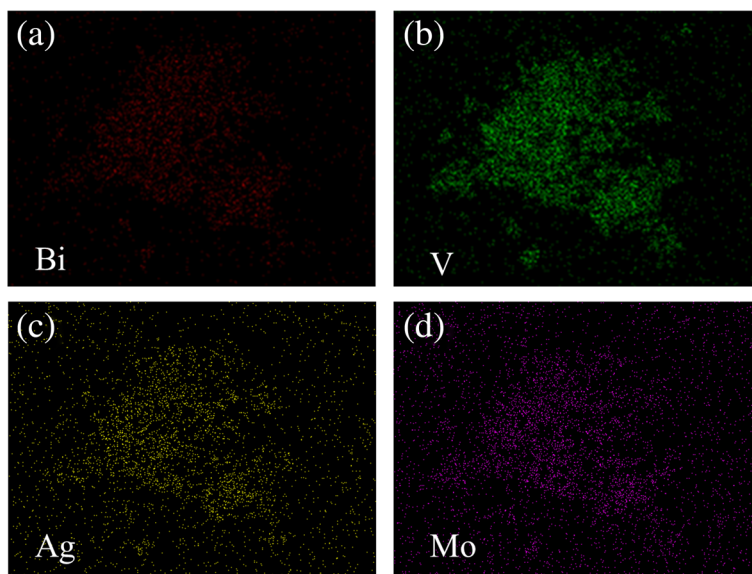


Fig. 2 a–d The corresponding elemental mapping analysis of Bi, V, Ag, and Mo in $\text{Ag/BiV}_{0.9925}\text{Mo}_{0.0075}\text{O}_4$, respectively

supernatant was measured in reference to the absorption intensity of RhB at 552 nm.

Characterization Techniques

The morphologies of the pure BiVO_4 and the decorated composites were investigated by field emission scanning electron microscopy (FESEM, S4800) and transmission electron microscopy (TEM; JEM-2100F, JEOL). Elemental analysis was performed by X-ray photoelectron spectroscopy (XPS; VGESCA-LAB MKII) with a non-monochromatic Mg $K\alpha$ X-ray source. The crystalline phase of the samples was determined by X-ray diffraction (XRD; Bruker D8) with Cu $K\alpha$ radiation. Inductively coupled plasma (ICP) was employed to analyze the elemental composition of the samples. Additionally, UV–vis diffuse reflectance spectrum measurements were performed using a Shimadzu spectrophotometer (UV-2450) to evaluate the bandgap energy of BiVO_4 , Ag/BiVO_4 , $\text{BiV}_{1-x}\text{Mo}_x\text{O}_4$, and $\text{Ag/BiV}_{1-x}\text{Mo}_x\text{O}_4$ over a wavelength range of 360–800 nm.

Results and Discussion

The crystallographic structure and phase of the prepared composites were characterized by XRD analysis (Fig. 1a).

The sharp diffraction peaks observed in the as-prepared BiVO_4 were assigned to the conventional BiVO_4 phase since they were in good agreement with the standard (JCPDS) card no. 14-0688. According to the peak splitting observed at 18.7° and 30.5° , which indicate the (110) and (040) facets, the prepared BiVO_4 material possessed a single monoclinic scheelite structure. A diffraction peak at 38.1° was observed in the Ag-related photocatalysts (Fig. 1a) corresponding to the (111) crystal phase of metallic Ag (JCPDS file: 65-2871). This indicates that the photoreduction of Ag^+ ions indeed occurred, leading to the deposition of Ag nanoparticles on the BiVO_4 and $\text{BiV}_{1-x}\text{Mo}_x\text{O}_4$ surfaces. Nevertheless, due to the low relative content of Ag, the XRD peaks were not intense.

As shown in Fig. 2a, EDS confirmed the presence of the Ag species, which agrees with the XRD results. The Bi (Fig. 2b), O (Fig. 2c), V (Fig. 2d), Mo (Fig. 2e), and Ag (Fig. 2f) elements are all distributed uniformly in the $\text{Ag/BiV}_{1-x}\text{Mo}_x\text{O}_4$ composites, and the results verify the existence of Mo and Ag. The relative amounts of Mo did not appear to affect the crystal structure or phase. The Mo substitution ratio was assessed by ICP (Table 1); the practical Mo atomic content was calculated to be 0.16% in $\text{Ag/BiV}_{0.9925}\text{Mo}_{0.0075}\text{O}_4$. It was observed that,

Table 1 Properties of the pure BiVO_4 , Ag/BiVO_4 , $\text{BiV}_{0.9925}\text{Mo}_{0.0075}\text{O}_4$, and $\text{Ag/BiV}_{0.9925}\text{Mo}_{0.0075}\text{O}_4$ powders

Sample	BiVO_4	Ag/BiVO_4	$\text{BiV}_{0.9925}\text{Mo}_{0.0075}\text{O}_4$	$\text{Ag/BiV}_{0.9925}\text{Mo}_{0.0075}\text{O}_4$
Bandgap (eV)	2.30	1.61	2.18	1.78
Atomic% of Ag dopant from ICP	–	6.28446	–	5.92476
Atomic% of Mo dopant from ICP	–	–	0.163704	0.167735
Atomic% of Ag dopant from XPS	–	6.03	–	4.72
Degradation rate (%)	6.4	8.4	9.6	97.9

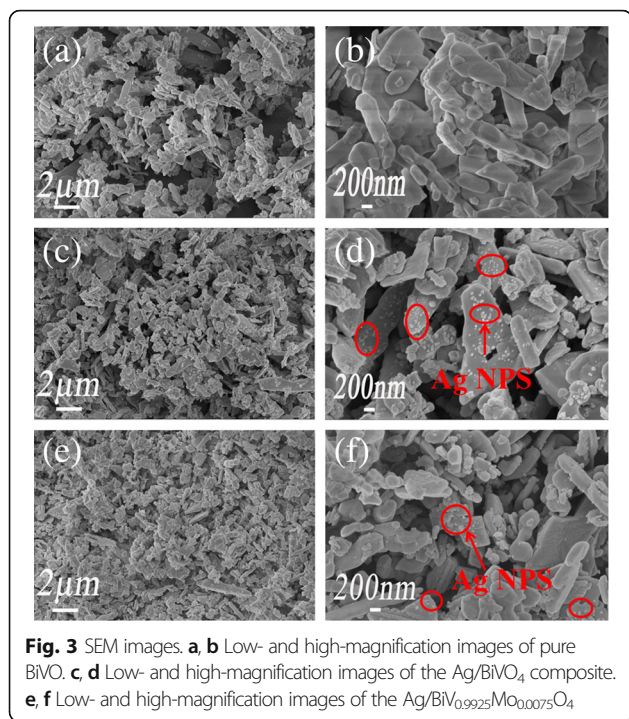


Fig. 3 SEM images. **a, b** Low- and high-magnification images of pure BiVO₄. **c, d** Low- and high-magnification images of the Ag/BiVO₄ composite. **e, f** Low- and high-magnification images of the Ag/BiV_{0.9925}Mo_{0.0075}O₄

although the nominal dopant content introduced with the precursors was 0.75%, the final resulting amount of Mo in the doped materials was always lower than the expected. Similar results have also been found in previous research, and it is possible that intrinsic losses and the evaporation of the Mo dopant occur during the hydrothermal synthesis processes [35, 36].

The morphology of the as-prepared pure BiVO₄, Ag/BiVO₄, and Ag/BiV_{1-x}Mo_xO₄ were investigated by SEM (Fig. 3). Pure BiVO₄ showed a slice-layer morphology with several clusters (Fig. 3a, b). For Ag/BiVO₄, metallic Ag was observed to be well dispersed on the (040) crystal facet (Fig. 3c), which agrees with the XRD analysis. The images of Ag/BiV_{0.9925}Mo_{0.0075}O₄ composite at different magnification were shown in Fig. 3e, d. Uniformly shaped metallic Ag nanoparticles were clearly observed on the surface of Ag/BiV_{0.9925}Mo_{0.0075}O₄ (Fig. 3d) likely due to the high exposure of the (040) surface. This crystal facet has been shown to have a good charge carrier mobility [37]. Thus, the observed morphology should be beneficial to the photocatalytic performance of the synthesized doped BiVO₄ powders. The as-prepared BiVO₄, Ag/BiVO₄, and Ag/BiV_{0.9925}Mo_{0.0075}O₄ samples were further observed by TEM (Fig. 4a). Interplanar spacings of 0.475 nm were clearly observed in Fig. 4b, corresponding to the (110)

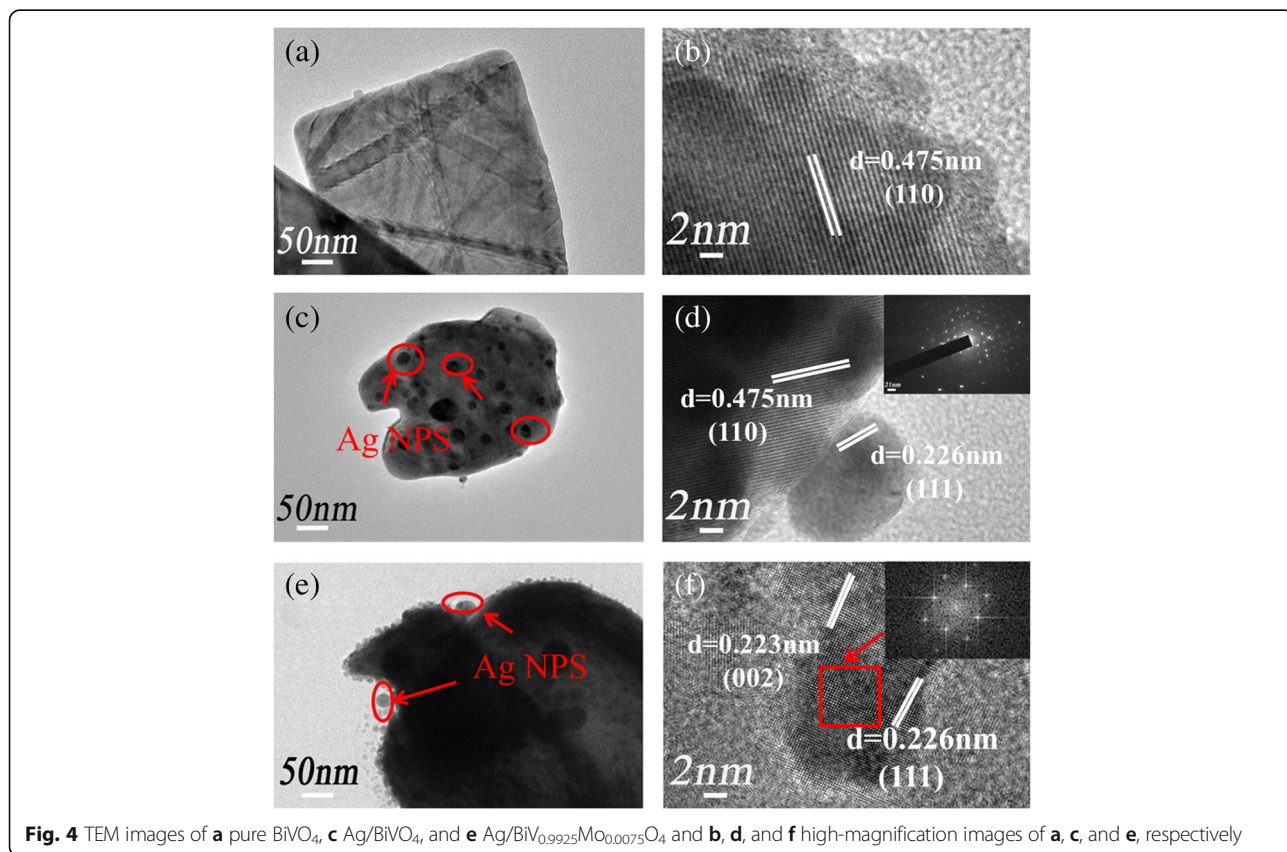
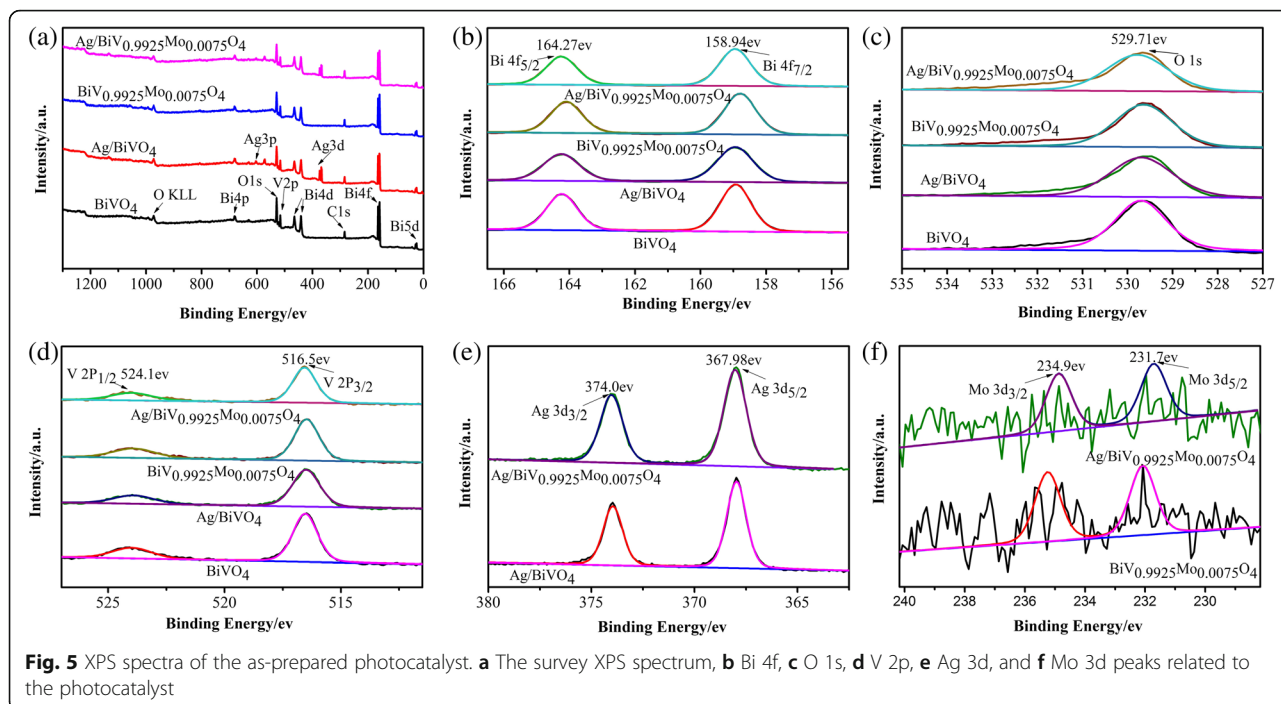


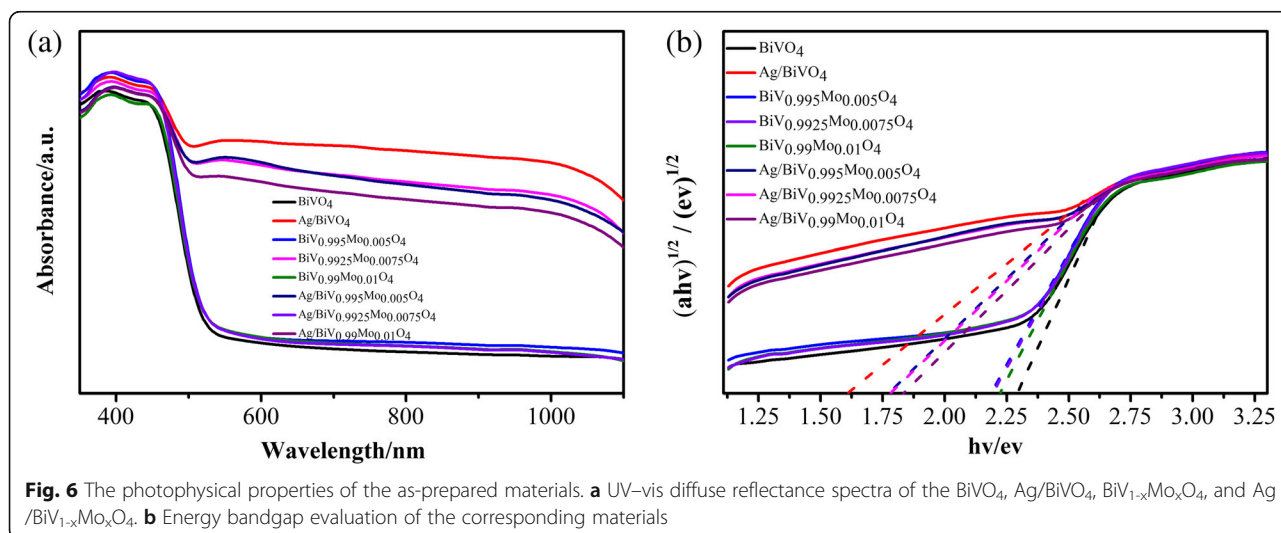
Fig. 4 TEM images of **a** pure BiVO₄, **c** Ag/BiVO₄, and **e** Ag/BiV_{0.9925}Mo_{0.0075}O₄ and **b, d,** and **f** high-magnification images of **a, c,** and **e**, respectively



crystallographic facet of BiVO₄ (JCPDS Card No. 14-0688). The crystal lattice fringe at 0.226 nm belonged to the (111) plane of metallic Ag nanoparticles in the Ag/BiVO₄ and Ag/BiV_{0.9925}Mo_{0.0075}O₄ samples (Fig. 4d, f). Based on the above analyses, metallic Ag was successfully deposited onto the BiV_{0.9925}Mo_{0.0075}O₄ surface, leading to a good connection between Ag and the Mo-doped BiVO₄ and promoting effective electron and hole separation in the composite system.

XPS analysis of the as-prepared samples confirmed the presence of Bi, V, O, Ag, and Mo (Fig. 5a). The binding energies of Bi 4f were 158.94 and 164.27 eV,

corresponding to Bi 4f^{7/2} and 4f^{5/2}, respectively, confirming the Bi³⁺ peaks in BiVO₄ (Fig. 5b). A typical O 1s spectrum was observed, as indicated by the main characteristic peak at 529.71 eV (Fig. 5c). The V 2p^{3/2} and 2p^{1/2} peaks observed at 516.5 and 524.1 eV, respectively, indicated the existence of V⁵⁺ (Fig. 5d). The Ag 3d peaks at 367.98 and 374.0 eV, corresponding to Ag 3d^{5/2} and 3d^{3/2} (Fig. 5e), respectively, were observed in both Ag/BiVO₄ and Ag/BiV_{0.9925}Mo_{0.0075}O₄, confirming the existence of the metallic Ag species. Furthermore, the molar ratio of metallic Ag species accounted for 6.6% of all elements, as determined by XPS and in agreement with



the ICP measurements (Table 1). Finally, the Mo 3d^{5/2} and 3d^{3/2} peaks located at 231.7 and 234.9 eV (Fig. 5f), respectively, confirm the presence of Mo⁶⁺.

UV–vis diffuse reflectance spectrum measurements were taken to evaluate the optical bandgap and absorption properties of the photocatalysts, as shown in Fig. 5. The photocatalytic activity of a semiconductor is largely dependent on the size of the bandgap; the narrower the bandgap is, the greater the shift is of the absorption wavelength towards longer wavelengths. The bandgap of as-prepared BiVO₄ was approximately 2.3 eV (Fig. 6b), which agrees with the Kubelka–Munk bandgap estimation theory [38]. Compared with BiVO₄, all the Mo-doped samples showed relatively narrow bandgaps (Fig. 6b). Furthermore, all Ag-deposited BiVO₄ and BiV_{1-x}Mo_xO₄ photocatalysts exhibited strong absorption in the visible light range in Fig. 6a. The Ag/BiVO₄ photocatalyst exhibited the best light absorption. The absorbance of as-prepared Ag/BiV_{0.9925}Mo_{0.0075}O₄ was between that of BiVO₄ and Ag/BiVO₄, thus indicating that the introduction of Mo hindered the photoresponsive characteristics of Ag. However, it is worth pointing out that, in addition to photoabsorption, other characteristics can also significantly influence the photocatalytic efficiency of photocatalysts.

Photoluminescence (PL) spectras were taken to investigate the separation efficiency of the photogenerated electron–hole pairs. The PL spectra of pure BiVO₄, BiV_{0.9925}Mo_{0.0075}O₄, Ag/BiVO₄, and Ag/BiV_{0.9925}Mo_{0.0075}O₄ composites, with an excitation wavelength of 310 nm, are shown in Fig. 7. BiVO₄ and BiV_{0.9925}Mo_{0.0075}O₄ show a prominent emission band centered at approximately 510 nm. The order of the intensity of the PL spectra was BiVO₄ > BiV_{0.9925}Mo_{0.0075}O₄ > Ag/BiVO₄ > Ag/BiV_{0.9925}Mo_{0.0075}O₄. Because a lower PL intensity

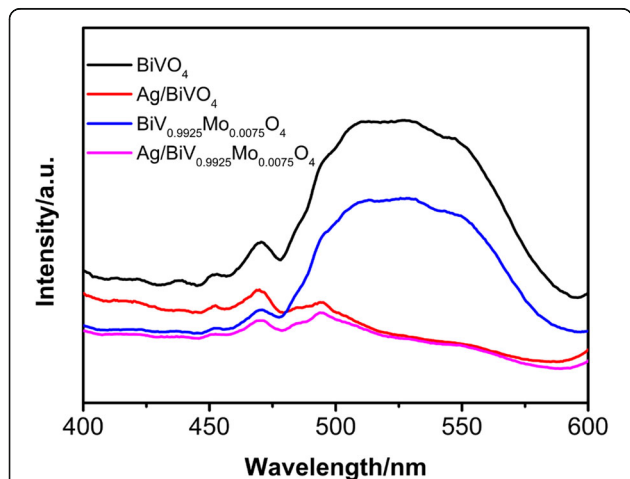


Fig. 7 Photoluminescence spectra of pristine BiVO₄, Ag/BiVO₄, BiV_{0.9925}Mo_{0.0075}O₄, and Ag/BiV_{0.9925}Mo_{0.0075}O₄ composites

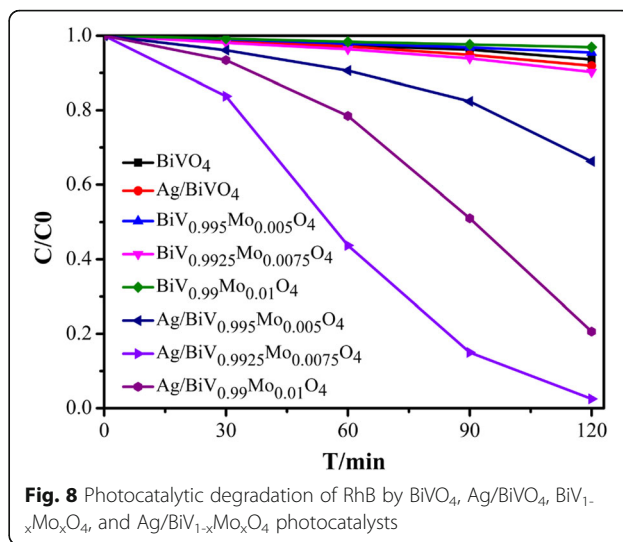


Fig. 8 Photocatalytic degradation of RhB by BiVO₄, Ag/BiVO₄, BiV_{1-x}Mo_xO₄, and Ag/BiV_{1-x}Mo_xO₄ photocatalysts

indicates a higher separation efficiency, this would lead to a higher photocatalytic activity in the overall system. Consequently, the higher photocatalytic performance of Ag/BiV_{0.9925}Mo_{0.0075}O₄ agrees with the PL measurement.

The photocatalytic decomposition results, according to the degradation of RhB under visible light ($\lambda > 420$ nm), confirmed Ag or Mo alone had little effect on the catalytic activity of BiVO₄ under light irradiation for 2 h (Fig. 8). Conversely, the deposition of Ag on Mo-doped BiVO₄ showed effective photocatalytic activity, with the variation of the Mo content, showing a difference in photocatalytic activity. Ag/BiV_{0.9925}Mo_{0.0075}O₄ exhibited an extremely efficient degradation of RhB under visible light irradiation with full decolorization after 2 h while only 7, 8, and 10% degradation was achieved over BiVO₄, Ag/BiVO₄, and BiV_{0.9925}Mo_{0.0075}O₄, respectively. Thus, Mo-doped Ag-deposited BiVO₄ was able to suppress the charge

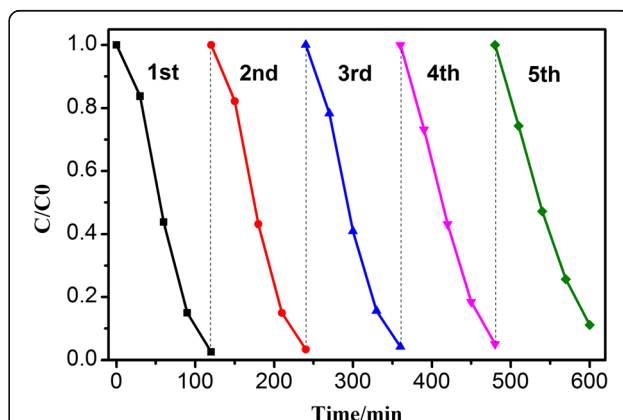


Fig. 9 Five cycle runs of Ag/BiV_{0.9925}Mo_{0.0075}O₄ for the photodegradation of RhB under visible light irradiation

recombination and greatly enhance the efficiency of the photocatalytic process.

The stability and reusability of photocatalysts are very important for their practical application. Therefore, we assessed the repeated cycles of Ag/BiV_{0.9925}Mo_{0.0075}O₄ in the photocatalytic degradation of RhB for 2 h under visible light irradiation. Overall, 99% of the RhB solution was degraded after five cycles (Fig. 9), indicating that the sample exhibited good photocatalytic stability.

To further assess the separation efficiency, the charge carrier lifetimes of pure BiVO₄, Ag/BiVO₄, and Ag/BiV_{0.9925}Mo_{0.0075}O₄ were also analyzed (Fig. 10). The

decay curves for the as-prepared photocatalysts fit well to a double-exponential function. The charge carrier decay lifetimes of BiVO₄, Ag/BiVO₄, and Ag/BiV_{0.9925}Mo_{0.0075}O₄ composites were 1.2304, 1.8220, and 2.0933 ns, respectively. Thus, the Ag-deposited samples, both with and without Mo doping, had much longer charge carrier lifetimes than pure BiVO₄, achieving effective photocarrier separation and suggesting that a synergistic effect among Ag, Mo, and BiVO₄ led to enhancements of the photocatalytic activity.

To explore the underlying photocatalytic mechanism, RhB degradation was conducted under visible light irradiation [39], adding a hole (h⁺) scavenger (ammonium oxalate ((NH₄)₂C₂O₄)), a superoxide radical (•O²⁻) scavenger (1,4-benzoquinone, BQ) [40], or hydroxyl radical (•OH) scavengers (tert-Butanol, t-BuOH) [41]. Following the addition of BQ, no obvious decrease was observed, but an acceleration in the degradation rate was detected compared to that of Ag/BiV_{0.9925}Mo_{0.0075}O₄ (Fig. 11). The faster degradation rate may have resulted from the SPR-effect of metallic Ag in Ag/BiV_{0.9925}Mo_{0.0075}O₄, which would enhance the separation efficiency of electrons and holes. However, when t-BuOH was added, the catalytic efficiency decreased from 97.5 to 78.1%, indicating the presence of •OH as the active species. The photocatalytic activity was drastically reduced with the addition of (NH₄)₂C₂O₄, suggesting that the holes acted as the main active species.

To further confirm the main active species generated in the photocatalytic process, electron spin resonance (ESR) was used. The principle of ESR is to react with free radicals using a spin-trapping agent to generate a relatively stable free radical adduct. A peak intensity was observed under visible light compared with dark conditions (Fig. 12a), demonstrating the existence of •O²⁻. In

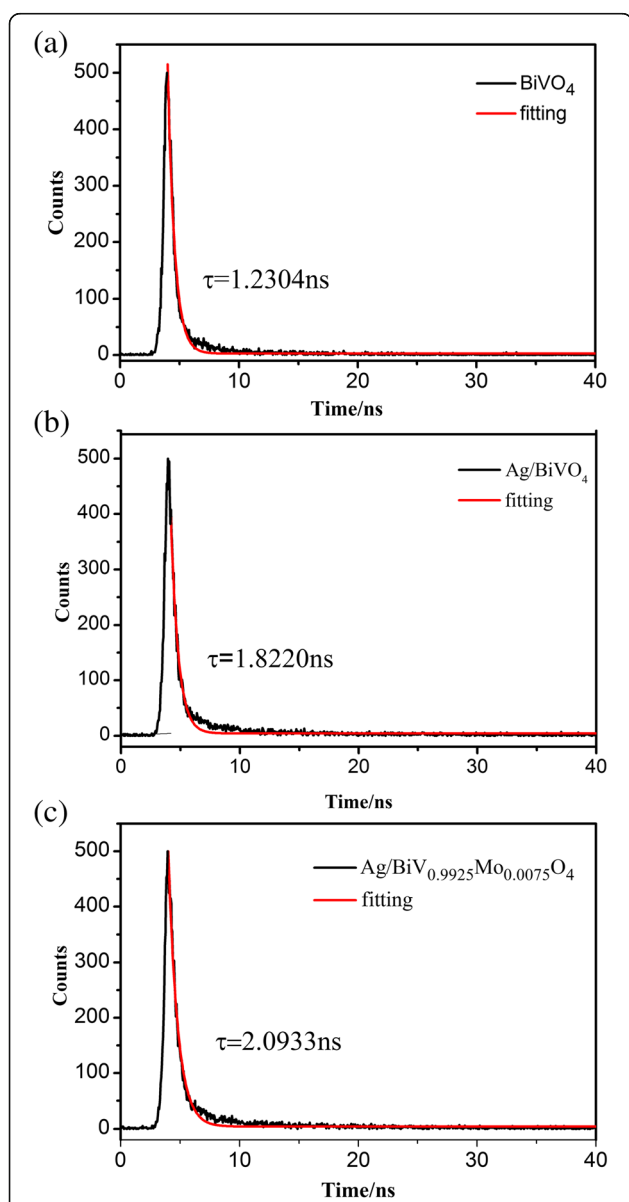


Fig. 10 ns-level time-resolved fluorescence decay curves of as-prepared **a** BiVO₄, **b** Ag/BiVO₄, and **c** Ag/BiV_{0.9925}Mo_{0.0075}O₄ composite

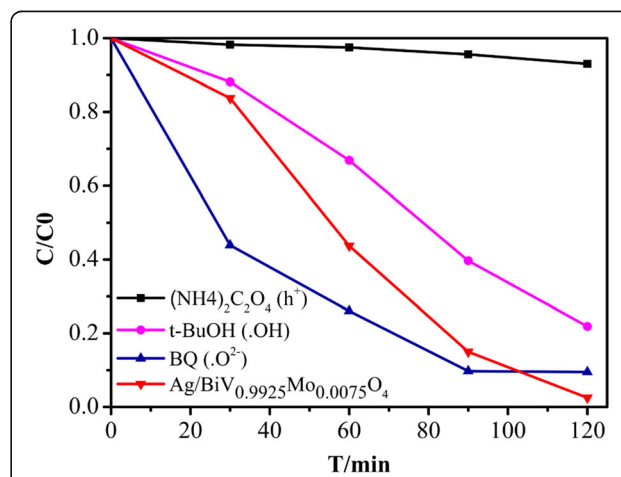
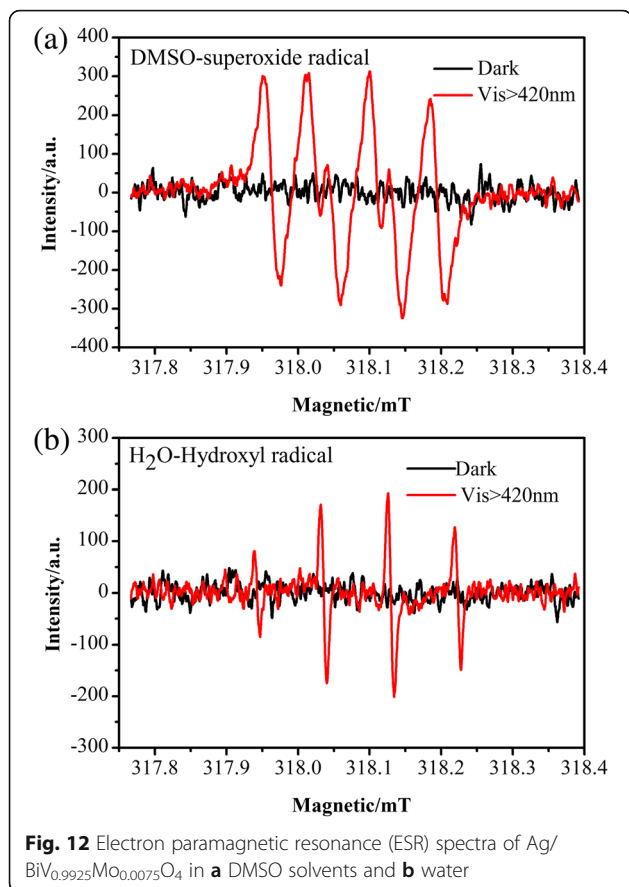


Fig. 11 Plots of photogenerated carrier trapping in the system during the photodegradation of RhB by Ag/BiV_{0.9925}Mo_{0.0075}O₄

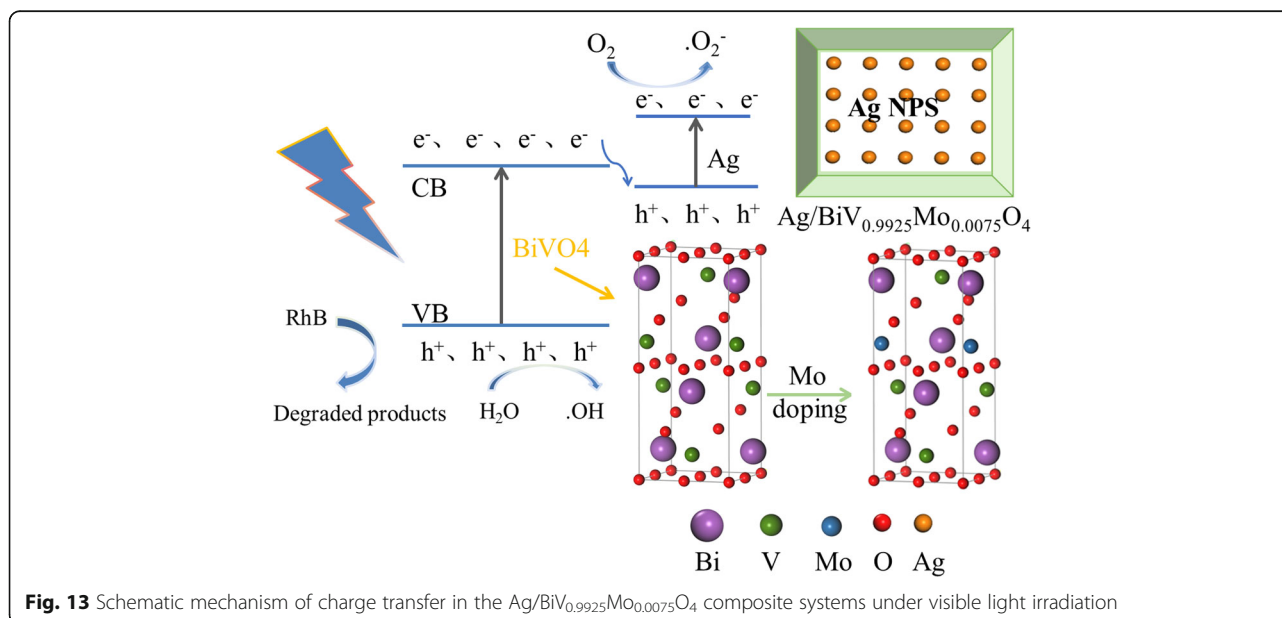


addition, obvious signals (Fig. 12b) suggested that •OH was produced in the photocatalytic process. In conclusion, the radical trap experiments and ESR analysis revealed that the photocatalytic process was governed by the combined effect of h⁺, •O²⁻, and •OH active species.

According to the discussion above, a possible photocatalytic mechanism of Ag/BiV_{0.9925}Mo_{0.0075}O₄ was illustrated in Fig. 13. The dopant Mo could effectively enhance the visible light absorption of the BiVO₄ photocatalyst. Ag/BiV_{0.9925}Mo_{0.0075}O₄ composite photocatalysts were irradiated under visible light, and the photoelectrons in the valence band of BiVO₄ could effectively jump to the conduction band to generate electron–hole pairs. The metallic Ag could accept the electrons, which then recombine with the photogenerated holes and enhance the transfer to the surface of the composite photocatalysts, resulting in the improvement of the separation of electrons and holes. The electrons could react to the O₂ and transform to •O²⁻. The holes of BiV_{0.9925}Mo_{0.0075}O₄ could react with the adsorbed H₂O molecules and transform to •OH. Meanwhile, the h⁺ could effectively react with the RhB, generating degraded products.

Conclusions

Herein, a simple hydrothermal synthesis procedure at almost neutral pH conditions and using ammonium carbonate as the structure-directing agent is reported for the preparation of Mo-doped BiVO₄ powders. Metallic Ag nanoparticles were then deposited on the (040) crystal facet of BiV_{0.9925}Mo_{0.0075}O₄. Thus, a photocatalytic system has been successfully constructed by means of the reduction reaction. These synthesis conditions have



been shown to significantly influence the increase in the size of the (040) crystallographic facet, as confirmed by XRD and STEM analyses. The XRD indicated that the peak splitting observed at 30.5° is a result of the (040) facets. Ag nanoparticles deposited on the (040) facets can also be seen from the STEM. Furthermore, Ag/BiV_{0.9925}Mo_{0.0075}O₄ showed a highly efficient photocatalytic performance for RhB degradation under visible light irradiation. This work could offer new inspiration for the rational utilization of BiVO₄ photocatalysts with high photocatalytic activity and their applications in the fields of energy production and environmental protection.

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Authors' contributions

XW and ZC conceived and designed the experiments. MY and SZ performed the experiments. XW, QM, MY, and GZ analyzed the data. XW contributed reagents/materials/analysis tools. All authors read and approved the final manuscript.

Competing interests

The authors declare that they have no competing interests.

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