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***In-situ* preparation of novel junction photocatalyst BiOBr/BiVO₄ with enhanced visible light photocatalytic activity**

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Heterojunction photocatalysts BiOBr/BiVO₄ were *in-situ* synthesized through acid etching coupled with hydrothermal process, and the optimized BiOBr/BiVO₄ ratio was tuned to explore their visible-light photocatalytic activity for MB degradation. Remarkably, BiOBr/BiVO₄ composites exhibited higher visible-light photocatalytic ability compared with single BiVO₄ and BiOBr alone. The charge-separation process was interpreted based on the energy band structure. The heterojunction formed between BiVO₄ and BiOBr, that effectively promotes the separation of photo-induced electrons and holes, is responsible for the improved photocatalytic activity.

1. Introduction

With energy crisis and increasing environmental problems, the green photocatalytic technology using solar energy exhibits great potential in degradation of organic pollutants. TiO₂, as a traditional photocatalytic material, displays excellent photocatalytic activity, but responding only to ultraviolet light (less than 5% of solar energy) due to its large band gap. Despite tremendous efforts made to broaden the visible-light response range, its capability to utilize the solar energy is still unsatisfactory.¹ To the end, the key to realize such purpose is designing and synthesizing new highly efficient visible-light photocatalysts. Fortunately, diverse visible-light responsive photocatalysts with a narrow band gap have been developed, such as WO₃,² BiVO₄,³ Bi₂WO₆⁴ and Fe₂O₃,⁵ amid which monoclinic bismuth vanadate (BiVO₄) emerges as one of the most popular materials owing to its appropriate band gap (2.4 eV), chemical stability and environmental friendly characteristics,^{6,7} and has experimentally demonstrated potential visible-light activity for the degradation of organic pollutants.^{8,9} The fast recombination of photo-induced electrons and holes, however, hinders its further gain when being employed alone. To solve this problem, one strategy is to manipulate the heterostructures by integrating BiVO₄ with noble metal nanoparticles¹² and/or other proper semiconductors with suitable band alignment such as BiVO₄/Co₃O₄,¹³ Cu₂O/BiVO₄,¹⁴ BiIO₄/BiVO₄,¹⁵ BiVO₄/g-C₃N₄¹⁶ etc. The charge carriers' recombination could be dramatically suppressed through the heterostructures, causing the higher carrier mobility and fast separation of electron-hole pairs.

Bismuth oxyhalides BiOX (X=Cl, Br, I) with a layered tetragonal matlockite crystal structure, were recently reported as efficient p-type photocatalysts for degrading pollutants.¹⁷⁻¹⁹ Interestingly, their band gaps decrease in the order of BiOCl, BiOBr, BiOI (~3.2 eV, ~2.7 eV, ~1.7 eV, respectively²⁰). BiOCl exhibited the exceptional photocatalytic property that was even higher than commercial P25 under UV irradiation. Nevertheless, it suffers the poor absorbency of solar energy

as TiO_2 . BiOI presents the best visible-light photocatalytic activity, which was offset by the poor chemical stability and low oxidation activity. BiOBr simultaneously exhibits better visible-light absorbance and photocatalytic oxidation ability as well as chemical stability, and has received tremendous attention.^{21, 22} BiOBr related heterostructures like BiOBr-CdS ²³ and BiOBr-BiOI ²⁴ all exhibited the excellent photocatalysis activity because of the unique layered feature of BiOBr and their efficient heterojunction structures. Given the band alignment agreement, it is highly expected that a p-n heterojunction between n- BiVO_4 and p- BiOBr could benefit both the visible-light absorption and the separation of photo-induced carriers.

In this study, BiOBr/BiVO_4 heterojunction photocatalysts were therefore synthesized for the first time by an *in-situ* acid etching method using hydrobromic acid (HBr) as an etching agent. *In-situ* preparation is a predominant approach in synthesizing composite materials, via which the intimate contact between two phases could be beneficial to the transfer and separation of photoinduced charges advantageous over the common deposition technologies.^{19, 25} Their photocatalytic activities were evaluated by degrading MB under visible light ($\lambda > 400\text{nm}$). The photocatalytic mechanism of BiOBr/BiVO_4 heterojunction was proposed based on the energy band structures and the reactive species.

2. Experimental

2.1. Materials

All chemicals (analytical purity) were commercially available and used without further purification.

2.2. Preparation of catalysts

BiVO_4 precursor with hollow morphology and ring structure was achieved by a hydrothermal method reported in literature.¹⁴ Briefly, 7.5 mmol $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ was dissolved in 3.3 M diluted nitric acid solution to get clear $\text{Bi}(\text{NO}_3)_3$ solution. Additionally, 7.5 mmol NH_4VO_3 and 1.5 g EDTA were dissolved in 15 mL of 4 M NaOH solution at 35°C to get transparent NH_4VO_3 solution. Then, the prepared NH_4VO_3 solution was dropwised into the above $\text{Bi}(\text{NO}_3)_3$ solution under stirring to obtain a stable yellow suspension. After the pH value was slowly adjusted to 7 with 2 M NaOH aqueous solution, the suspension was transferred into a 50 mL Teflon-lined stainless steel autoclave and heated at 180°C for 24 h. Finally, the product was centrifuged, washed with deionized water and ethanol, and dried at 80°C in air to yield the BiVO_4 precursor.

Heterojunction photocatalysts BiOBr/BiVO_4 were synthesized via a simple acid etching method in a hydrothermal process. 0.276 g of BiVO_4 powder was dispersed in 80 mL of HBr solution (8.00 mM) and then vigorously stirred for 1 h. The attained mixture was transferred into a 100 mL Teflon-lined stainless steel autoclave and heated at 180°C for different periods (17 h, 24 h, 31 h). The precipitates were centrifuged, washed with deionized water and dried at 80°C in air to obtain BiOBr/BiVO_4 heterojunction catalysts. In addition, single BiVO_4 and BiOBr were prepared by repeating the hydrothermal process (180°C , 24 h) except replacing HBr solution by deionized water and BiVO_4 powder by 1 mmol $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, respectively.

2.3. Characterization of catalysts

The crystal structures of the prepared samples were recorded by D/MAX-RB X-ray powder diffraction (XRD, Rigaku, Japan) with Cu K α radiation ($\lambda=0.15405$) at 40 KV and 30 mA. The morphologies and microstructures were observed by a scanning electron microscopy (SEM, JEOL JSM-6510A, Japan) at 5.00 KV and 10 mA, and a transmission electron microscopy (TEM, JEM-2100, Japan). The chemical status of Bi, O, V and Br was determined by a X-ray photoelectron spectroscopy (XPS, AXIS ULTRA^{DLD}, Kratos, Japan) with an Al K α line. UV-vis diffuse reflectance spectra (DRS) were carried out on a U-3900H UV-vis spectrophotometer (Hitachi, Japan) equipped with an integrating sphere attachment in the 400-800 nm range. The photoluminescence (PL) spectra were detected using F-4500 fluorescence spectrophotometer (Hitachi, Japan) with the excitation wavelength of 278 nm.

2.4. Photocatalytic activity measurements

The photocatalytic activities of as-prepared samples were estimated by the degradation of MB solution (10 mg/L, neutral condition) under visible-light at room temperature. A 100 W incandescent lamp was used as the light source (with a cutoff filter ($\lambda>400$ nm)). The distance between the light source and the reactor is fixed to be 5 cm. The suspension containing 50 mg photocatalyst sample in 50 mL MB aqueous solution was magnetically stirred for 1 h in the dark to reach an adsorption-desorption equilibrium before exposed to the light. At given irradiation time intervals of 1 h, 5 mL suspension was sampled and centrifuged. The concentration of supernatant was determined by Hitachi UV-vis spectrophotometer (U-3900H) at 664 nm. The degradation efficiency of MB was evaluated via the ratio of C/C_0 , where C was the concentration of MB during the reaction and C_0 was the initial concentration.

3. Results and discussion

3.1. Characterization of photocatalysts

XRD Analysis. Fig. 1 shows the XRD patterns of as-prepared BiVO₄, BiOBr, and BiOBr/BiVO₄ samples. For pure BiVO₄ and BiOBr, the diffraction peaks coincide with the standard monoclinic BiVO₄ (PDF card 14-0688, JCPDS) and the tetragonal BiOBr phase (PDF card 09-0393, JCPDS), respectively. No other peaks are observed, indicating both the high purity and the good crystallization. In BiOBr/BiVO₄ composites, the monoclinic BiVO₄ is dominant in all patterns. Feature peaks for BiOBr are undetectable due to the small quantity until the time reaches 31 h (BiOBr/BiVO₄-31h), where BiOBr could be apparently observed. There are no impurity peaks appeared other than BiVO₄ and BiOBr. The result suggests that BiOBr indeed formed by etching BiVO₄ in HBr under hydrothermal condition.

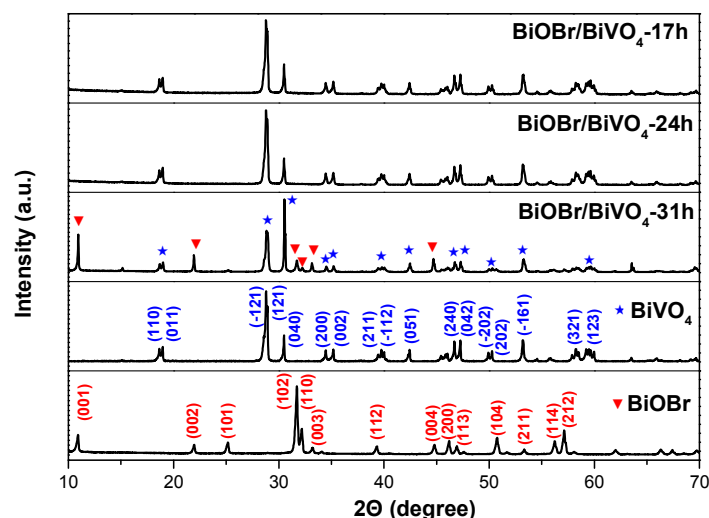


Fig. 1 XRD patterns of as-prepared samples.

3.1.2. XPS Analysis. The surface chemical composition and their chemical states of composites were analyzed by XPS, and were calibrated with surface C $1s$ at 284.8 eV (Fig. 2). The surface survey spectrum indicates the presence of Br, Bi, C, V, O elements in BiOBr/BiVO₄-24h (Fig. 2a). The carbon peak might originate from adventitious carbon on the surface of sample or hydrocarbon in the XPS instrument. The high resolution XPS spectra of the main composite elements, Bi $4f$, V $2p$, O $1s$ and Br $3d$, are presented in Fig. 2b-e. Two strong peaks located at 164.31 eV and 158.99 eV (Fig. 2b) separately are assigned to Bi $4f_{5/2}$ and Bi $4f_{7/2}$ of Bi³⁺ cation in BiOBr and BiVO₄.^{17, 26, 27} As shown in Fig. 2c, two peaks centered at 524.52 eV and 516.66 eV correspond to V $2p_{1/2}$ and V $2p_{3/2}$, respectively of V⁺⁵.²⁸ As for the O $1s$ (Fig. 2d), the XPS signal at a binding energy of 529.72 eV arises from O²⁻ anion in the lattice of BiOBr/BiVO₄.^{28, 29} Moreover, the Br $3d$ peak at 69.14 eV indicates the presence of Br⁻¹ in the composite, which is characteristic of bromine element in BiOBr.³⁰

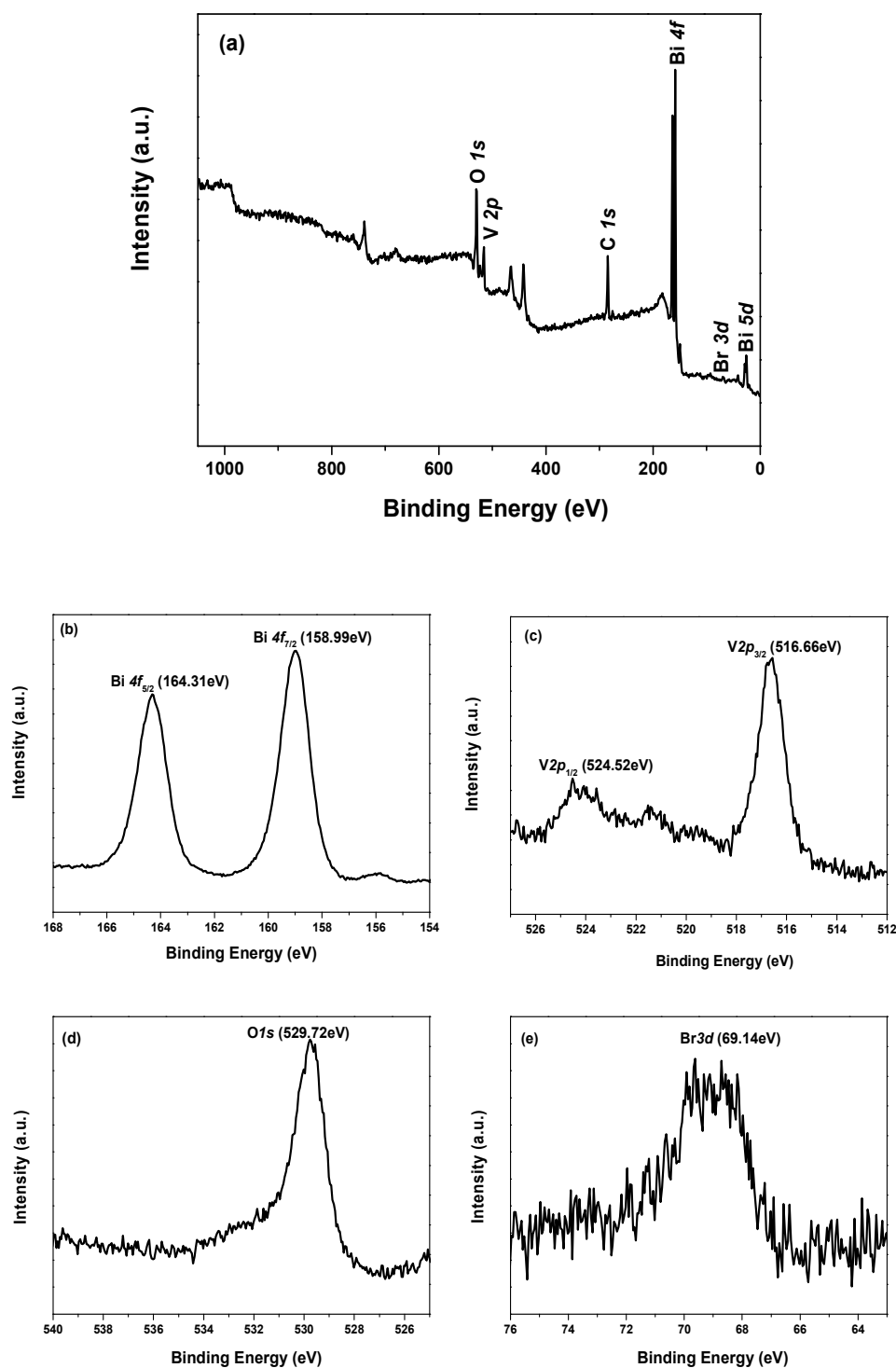


Fig. 2 XPS spectra of BiOBr/BiVO₄-24h sample: (a) surface survey spectrum, (b) Bi 4f, (c) V 2p, (d) O 1s, and (e) Br 3d.

3.1.3. SEM and TEM Analysis. The morphology of as-prepared samples was observed by SEM and shown in Fig. 3. The pure BiVO_4 presents cylindrical structure with smooth and clean surfaces (Fig. 3a), while BiOBr exhibits an irregular sheet shape (Fig. 3b). In $\text{BiOBr}/\text{BiVO}_4$ composite (Fig. 3c), it is clear that a certain amount of tiny particles distribute on the surface of BiVO_4 . This geometry could be more clearly observed from the TEM images of pure BiVO_4 crystal and $\text{BiOBr}/\text{BiVO}_4$ composite in Fig. 4 (a and b). The EDX analysis on the marked circles in Fig. 4(b) indicates that the tiny particle is composed of Bi, O, and Br elements and proven to be BiOBr , while the substrate composed of Bi, O, and V is assigned to be BiVO_4 (Fig. 4c and 4d). More importantly, the HRTEM image of $\text{BiOBr}/\text{BiVO}_4$ -24h heterogeneous nanostructure (Fig. 4(e)) shows that there are a uniform layer of BiOBr crystalline nanoparticles with the size of 5-8 nm in diameter growing on the substrate. The interplanar spacings of 0.308 nm, 0.276 nm and 0.285 nm correspond to the (121) planes of monoclinic BiVO_4 and (110), (102) planes of tetragonal matlockite BiOBr , respectively. Combining the XRD and XPS analysis, it could be safely concluded that the etching of BiVO_4 in HBr is accomplished in company with the *in-situ* growth of BiOBr nanoparticles that tightly anchored on the surface of BiVO_4 to form the heterojunction.

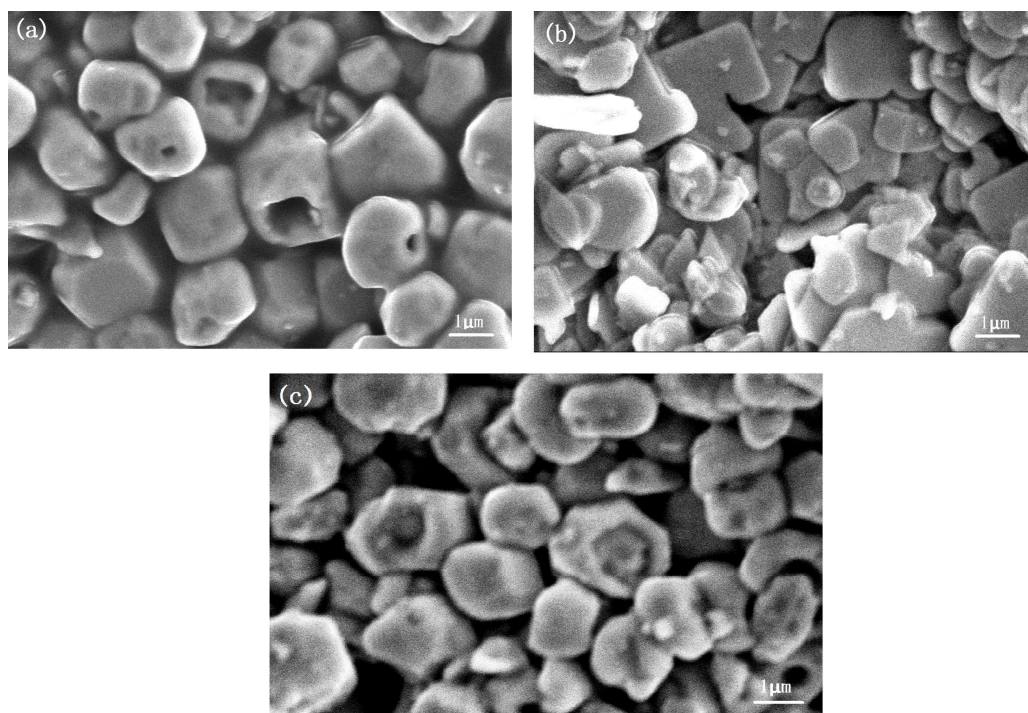


Fig. 3 SEM images of (a) BiVO_4 , (b) BiOBr , (c) $\text{BiOBr}/\text{BiVO}_4$ -24h.

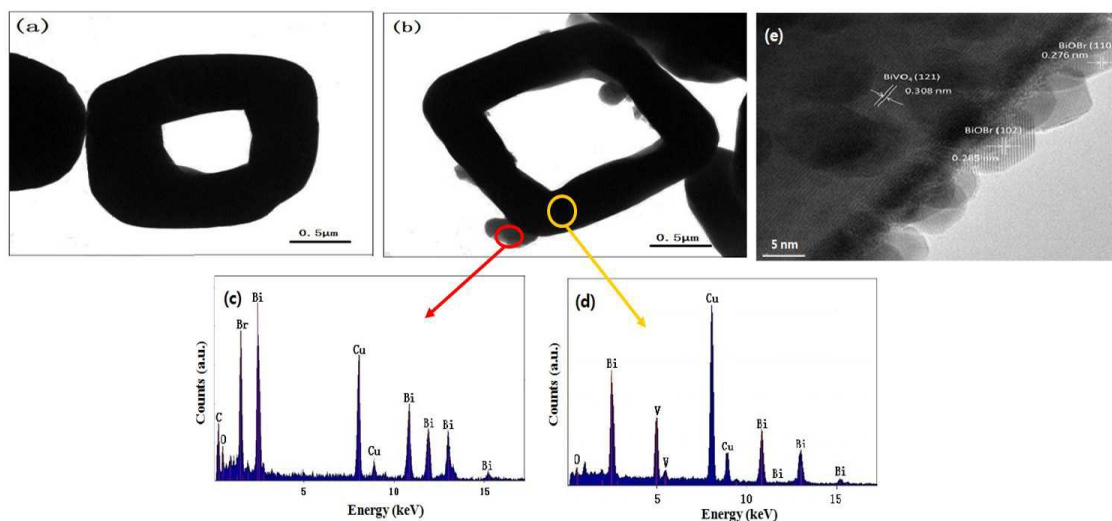


Fig. 4 TEM images of (a) BiVO_4 , (b) $\text{BiOBr/BiVO}_4\text{-24h}$, (c and d) EDX analysis of the part marked with red and yellow circles in Fig.4(b) and (e) HRTEM image of $\text{BiOBr/BiVO}_4\text{-24h}$.

3.1.4. UV-Vis DRS Analysis. Fig. 5 displays the UV-vis DRS of BiVO_4 , BiOBr and BiOBr/BiVO_4 composite samples. The E_g of as-prepared semiconductor photocatalysts are as well calculated using the following formula:³¹

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

where, α stands for the absorption coefficient; h is the Planck's constant; ν is the light frequency; A is a constant and E_g stands for the bandgap energy. The type of optical transition of a semiconductor is the determinants of n ($n=1$ for the direct semiconductor (BiVO_4) and $n=4$ for the indirect semiconductor (BiOBr)).³²⁻³⁴ Therefore, the corresponding E_g of BiVO_4 and BiOBr can be determined from a curve of $(\alpha h\nu)^{2/n}$ versus energy ($h\nu$). Since all BiOBr/BiVO_4 composites present similar absorption characteristics to pure BiVO_4 and the contents of BiOBr are low, n was assumed to be 1.

Clearly, BiOBr has an absorption edge at 450 nm, corresponding to a band gap of 2.76 eV; while BiVO_4 exhibits better visible light absorption up to 516 nm. Compared with pure BiVO_4 , all BiOBr/BiVO_4 heterojunctions exhibit higher visible light absorption ability. With increasing BiOBr content, the absorption intensity of BiOBr/BiVO_4 enhanced gradually. All the BiOBr/BiVO_4 series have a similar band gap of ~ 2.38 eV, which was close to pure BiVO_4 .^{33,35} This means the increase in the light absorption mainly stems from the scattering effect due to the presence of tiny BiOBr on BiVO_4 .

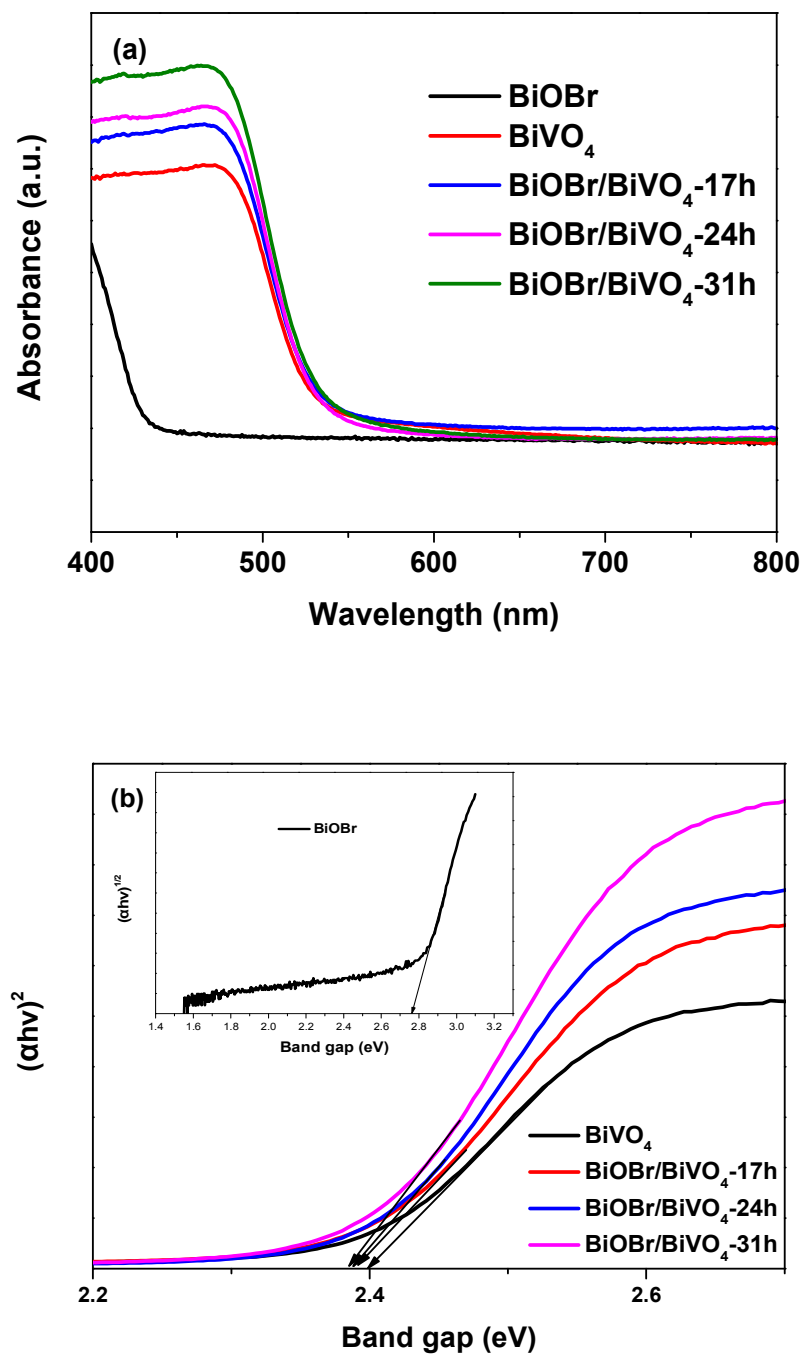


Fig. 5 (a) UV-DRS of as-prepared samples and (b) the band gaps energies of different samples: the plot of $(\alpha h\nu)^2$ versus energy ($h\nu$) of BiVO₄ and BiOBr/BiVO₄; the plot of $(\alpha h\nu)^{1/2}$ versus energy ($h\nu$) of BiOBr.

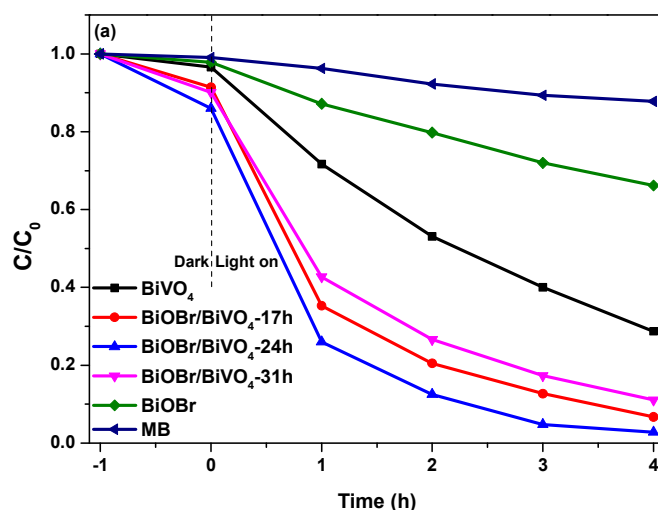
3.2. Photocatalytic properties

3.2.1. Photocatalytic activity. The photocatalytic performance of as-prepared BiVO₄, BiOBr, and BiOBr/BiVO₄ composites were evaluated by the degradation of MB under visible light ($\lambda > 400$ nm). The results are shown in Fig. 6(a). Self-degradation of MB under visible-light irradiation was negligible due to the high stability of MB. The adsorption of dye on the photocatalyst surface had a great influence on the degradation effect. It is observed that all the samples presented the similar low capacity for the dye adsorption in dark, indicating that the dye fading mainly resulted from photocatalytic degradation. Under the visible-light irradiation, all BiOBr/BiVO₄ composites exhibited highly pronounced photocatalytic performance compared to single BiVO₄ and BiOBr alone. The photocatalytic activity reaches a maximum at BiOBr/BiVO₄-24h with a photodegradation rate of 97.2% after 4 h of irradiation, and then drops off with more increased loading level. It suggests that although BiOBr/BiVO₄ heterojunction is supposed to suppress the recombination of photo-induced electron-hole pairs, the excessive BiOBr may act as recombination centers to consume the charge carriers.

In order to directly present the reaction kinetics of MB degradation, the photocatalytic process is quantitatively expressed using the pseudo-first-order kinetics equation:

$$\ln(C_0 / C) = kt + \alpha,$$

where, k is the pseudo-first-order rate constant. The kinetic parameters of all photocatalysts are calculated and listed in Fig. 6(b). BiOBr/BiVO₄-24h sample had the best photodegradation activity with a k value of 0.85006 h⁻¹, ~2.8 times that of BiVO₄ (0.30086 h⁻¹) and ~8.7 times that of BiOBr (0.09726 h⁻¹).



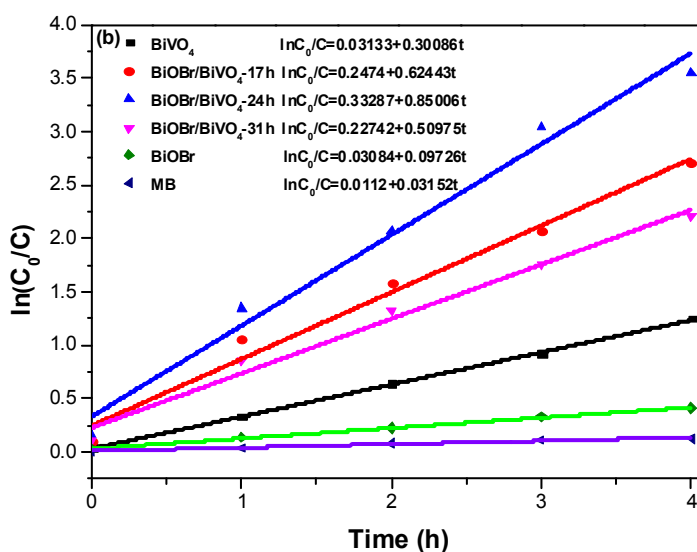


Fig. 6 (a) Photocatalytic degradation efficiency of MB by as-prepared samples under visible light irradiation and (b) the kinetics of degradation of MB over different samples.

3.2.2. Photostability. The stability of BiOBr/BiVO₄-24h was evaluated by repeating degradation experiments of MB. After each run, the photocatalyst was centrifuged, washed with deionized water, and then, the concentrated MB solution was re-injected into the separated sample to carry out photocatalytic test. As shown in Fig. 7 (a), the photocatalytic activity of BiOBr/BiVO₄-24h in the 2nd and 3rd run debase slightly compared with the 1st run. This may be caused by a very small quantity of residual undegraded dye molecules or intermediates adsorbed on the surface of the photocatalyst during the 1st run.³⁶ However, the degradation rates in the 2nd and 3rd run were almost same, which indicates that the BiOBr/BiVO₄ heterojunction photocatalysts are stable in the degradation of organic pollutants. Moreover, the XRD analysis of the photocatalysts before and after the photoreaction experiment further confirms the relative stability of the catalysts now that no notable change in the XRD patterns is observed between the fresh and used samples (Fig. 7 (b)).

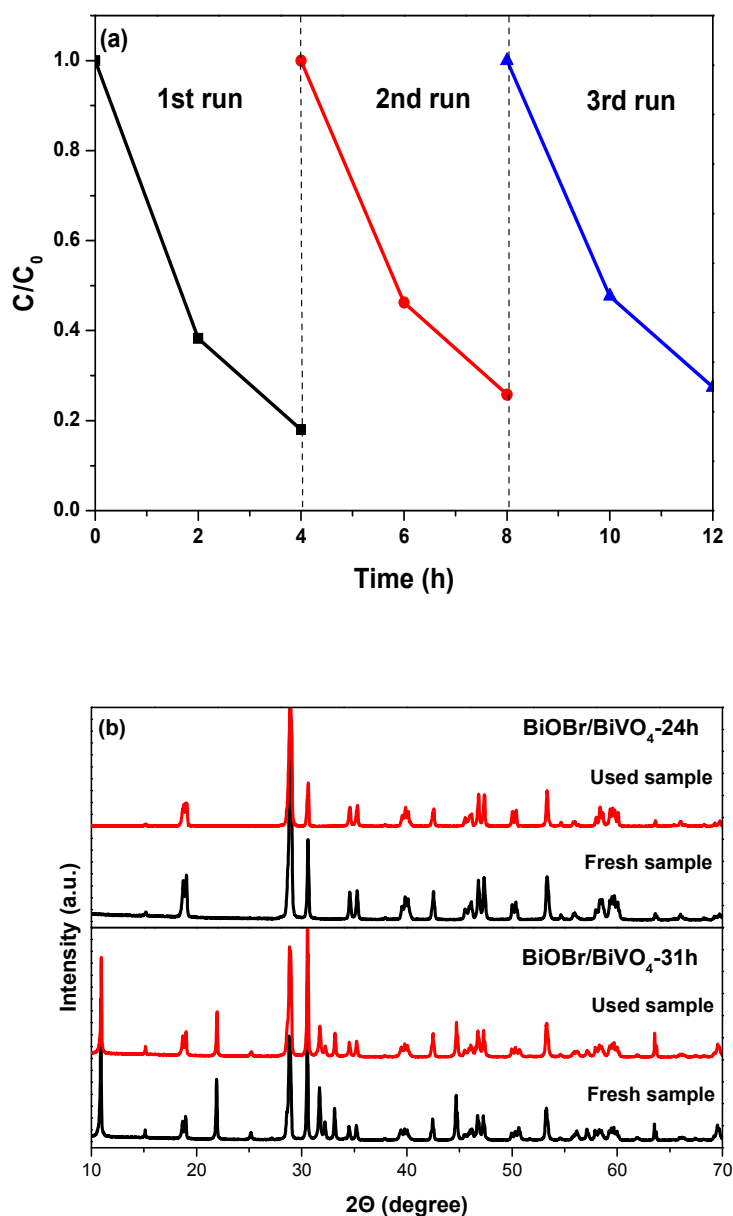


Fig. 7 (a) Cyclic degradation curve of MB in the presence of BiOBr/BiVO₄-24h and (b) XRD patterns of the photocatalysts before and after the photoreaction experiments.

3.3. Possible photocatalytic mechanism

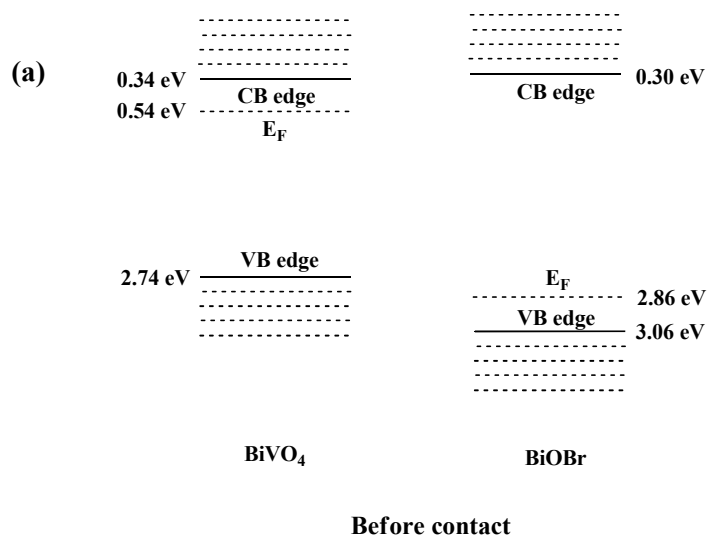
It is crucial for a heterojunction illustrating better photocatalytic performance that the each involved component must have a favorable band alignment with its counterparts. To understand the electronic band structure between BiVO₄ and BiOBr, the CB and VB potentials of BiOBr and BiVO₄ were estimated by the following empirical formulas,

$$E_{CB} = \chi - E^e - 0.5E_g \quad (1)$$

$$E_{VB} = E_{CB} + E_g \quad (2)$$

where, E_{CB} and E_{VB} are the CB and VB edge potentials; E_g is the band gap energy of semiconductors, calculated from the DRS (Fig. 5b); χ is the electronegativity of a semiconductor (6.04 eV³³ and 6.18 eV³⁷ for BiVO₄ and BiOBr, respectively); E^e is the energy of free electrons on the hydrogen scale (4.5 eV). Accordingly, the E_{CB} and E_{VB} of two semiconductors were calculated to be 0.34 eV and 2.74 eV for BiVO₄, 0.30 eV and 3.06 eV for BiOBr, respectively, as schematically illustrated in Fig. 8a. Generally, the Fermi level is located below the CB by 0.1-0.2 eV for an *n*-type semiconductor, while above the VB by 0.1-0.2 eV for a *p*-type semiconductor.³⁸ Therefore, the Fermi Level is fixed at approximately 0.54 eV for *n*-BiVO₄ and 2.86 eV for *p*-BiOBr (0.2 eV was chosen in the study), respectively.

When *p*-BiOBr and *n*-BiVO₄ were brought together to form a *p-n* heterojunction, a depletion layer could be created at the interface that leads to the formation of an internal static electric field. Meanwhile, Fermi levels shift to reach an energetic equilibration. Owing to the low BiOBr content in the composites, the ultimate Fermi level of such heterojunction should approach to around 0.54 eV close to that of BiVO₄. This means energy bands of BiOBr will move forward along the Fermi level and generate the band bending at the interface to generate a type II *p-n* heterojunction. A possible schematic band alignment diagram in such heterostructure is shown in Fig. 8b. On the one hand, BiOBr cannot block the visible light harvesting by BiVO₄ because BiOBr is transparent for that wavelength range, instead improve the light absorption of BiVO₄ due to scattering as demonstrated in Fig. 5a. On the other hand, both the band alignment between BiVO₄ and BiOBr and the internal electric field at the interface are favorable for charge separation.





To confirm this effect, PL test was performed, as shown in Fig. 9 Generally, the relatively lower PL intensity means the lower recombination rate of electron-hole pairs and thus the higher photocatalytic activity. Clearly, the PL intensity of BiOBr/BiVO₄ composites notably decrease compared with pure BiVO₄, which demonstrates that the heterojunction formed between BiOBr and BiVO₄ effectively improves the charge separation and suppresses the charge recombination.

Photocatalytic reaction includes four basic processes: light absorption, charge separation, migration, and recombination. The survived charge carriers (holes and electrons) diffuse to the surface and participate in the chemical reactions through generating reactive species $\cdot\text{O}_2^-$ and $\cdot\text{OH}$, as well as h^+ , which ultimately photocatalytically degrade the organic substances. In order to confirm the function of three reactive species in this study, different scavengers, benzoquinone (BQ),³⁹ isopropyl alcohol (IPA),⁴⁰ and ammonium oxalate (AO),⁴¹ were employed to trap $\cdot\text{O}_2^-$, $\cdot\text{OH}$ and h^+ , respectively. The corresponding ultimate concentrations of BQ, IPA and AO in the reaction were 0.3 mmol/L, 1.0 mmol/L and 1.0 mmol/L, respectively. Meanwhile, the experiment without scavenger was also performed. With adding any scavenger, the degradation rate declined (Fig. 10), which suggests that $\cdot\text{O}_2^-$, $\cdot\text{OH}$ and h^+ all played key roles in the MB degradation. Based on the experimental data, the function of active species decreased according to the following order: $\text{h}^+ > \cdot\text{O}_2^- > \cdot\text{OH}$.

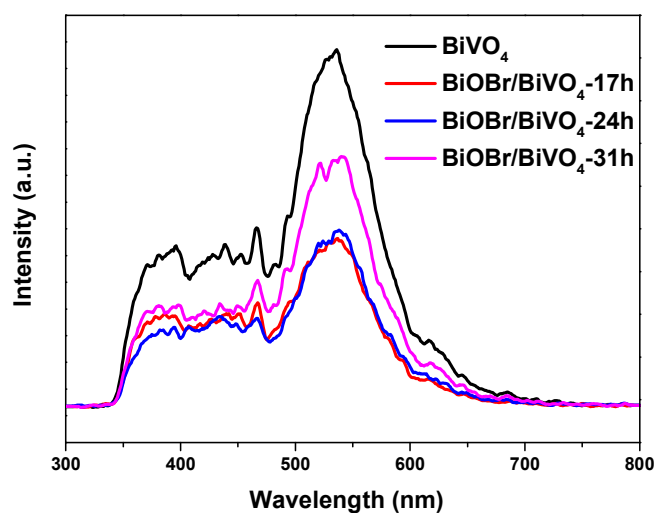


Fig. 9 PL spectra of pure BiVO_4 and BiOBr/BiVO_4 samples ($\lambda_{\text{ex}} = 278 \text{ nm}$)

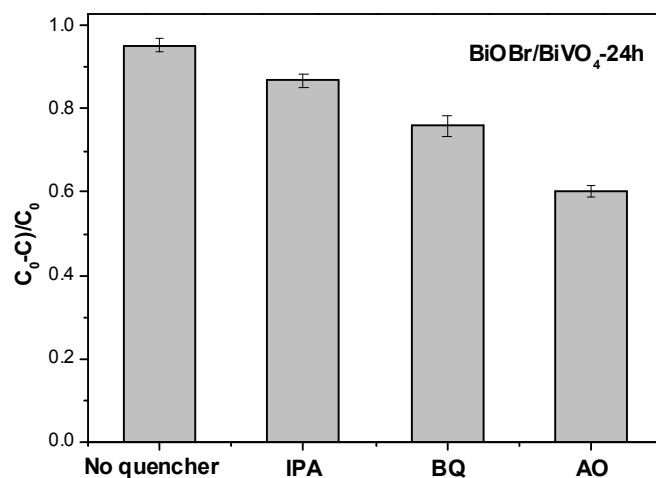
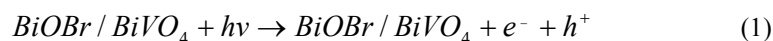


Fig. 10 Trapping experiments of active species on the degradation of MB in the presence of $\text{BiOBr/BiVO}_4\text{-24h}$

As discussed above, a quantity of holes transferred to the VB of BiOBr. Since the VB (0.74 eV) of BiOBr is less positive than $E(\cdot\text{OH}/\text{OH}^-)$ (2.38 eV),³² however, the holes on the VB of BiOBr couldn't be able to oxidize $\text{OH}^-/\text{H}_2\text{O}$ to $\cdot\text{OH}$. Instead most of the photogenerated holes directly oxidized MB adsorbed on the surface of BiOBr/BiVO_4 composites. This pathway predominates in degradation process of MB, which is consistent with the trapping experiment. While, the small quantity of holes in the VB of BiVO_4 possessing strong oxidizing ability due to their high positive potential (2.74 eV) could oxidize OH^- and H_2O to $\cdot\text{OH}$ and then degrade MB.

Furthermore, it is possible that the electrons in the VB of BiVO₄ could be excited to the higher positions besides the bottom positions of the CB.⁴¹⁻⁴⁴ These electrons could also reduce O₂ to •O₂⁻ to degrade MB. Thus, h⁺, •O₂⁻ and •OH all contributed to the degradation but the function decrease in turn, which is consistent with trapping experiments well. A possible pathway of photocatalytic reaction can be proposed as follows:



4. Conclusions

In summary, BiOBr/BiVO₄ heterojunction photocatalysts were successfully synthesized using acid etching under hydrothermal condition. The XRD, XPS and morphological studies reveal that BiOBr tiny particles grew tightly on the surface of monoclinic BiVO₄. The as-prepared BiOBr/BiVO₄ composites displayed much higher photocatalytic activity than pure BiOBr and BiVO₄ for MB removal under visible light irradiation ($\lambda > 400\text{nm}$) and owned good photocatalytic stability. The enhanced photocatalytic activity of the composites is attributed to the formation of heterojunctions between BiOBr and BiVO₄, which effectively improve the separation of photoinduced electron-hole pairs. Active species h⁺, •O₂⁻ and •OH all contribute to the degradation of MB.

Acknowledgments

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Heterojunction photocatalysts BiOBr/BiVO₄ were *in-situ* synthesized through acid etching coupled with hydrothermal process and they displayed higher photocatalytic activity than pure BiOBr and BiVO₄ for MB removal under visible light irradiation.

