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Enhanced visible light photocatalytic activity of AgBr on {001} facets exposed to BiOCl



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ABSTRACT

The facet dominated AgBr/BiOCl composites with exposed {001} (BiOCl-001) and {101} (BiOCl-101) facets were prepared by facile solvothermal and chemical precipitation process. Microstructures, morphologies, photoelectron and band gap energy of the as-prepared composites were characterized by various experimental methods. The AgBr/BiOCl heterojunctions showed a much higher photocatalytic performance than pure AgBr and BiOCl in photodegradation of Rhodamine B (RhB) under visible light irradiation. In addition, the AgBr-{001}BiOCl with the mole ratio of 1:2 showed the highest photocatalytic performance with the RhB completely degraded in 15 min. The better photocatalytic performance of AgBr-{001}BiOCl may attribute to the fact that {001} facet of BiOCl was beneficial for the separation of photo-generated carriers and more oxygen vacancy can be formed on the surface {001} facets of BiOCl. Moreover, the photocatalytic mechanism of AgBr-{001}BiOCl composites were also discussed.

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1. Introduction

Semiconductor photocatalysis is a promising technology using solar light energy through storing photon energy in the chemical bonds to mitigate the environment deterioration and alleviate the energy crisis, therefore it has attracted much more attention for its wide application. Over the past several years, BiOCl has drawn considerable interests for its unusual electrical and optical properties [1–4]. Besides, excellent photocatalytic properties have been obtained on BiOCl and their compounds under ultraviolet or visible light illumination. For instance, Bismuth oxychloride (BiOCl) exhibits higher activity for organic dyes degradation than TiO₂ under UV light illumination due to its unique layer structure [5-7]. Recently, some researchers reported that BiOCI nanosheets with highly exposed {001} facets displayed more excellent photocatalytic activity under ultraviolet irradiation, which is mainly due to the fact that the {001} facets might facilitate the generation of oxygen vacancies [8]. Furthermore, it has been exhibited that the density of oxygen (O) atoms on {001} facets of bismuth oxychloride was much bigger than on other facets [9]. However, the wide bandgap (3.5 eV) of BiOCl limits its further application in visible

light region [2], and the rapid recombination of photo-generated electrons and holes makes it far from satisfaction. Therefore, it is highly demanded to tailor BiOCl semiconductor materials with suitable method to improve its photocatalytic activity under visible light irradiation. In previous reports, Hu et al. have selectively synthesized BiOCl nanoplates with exposed {001} and {102} facets by adding sodium citrate via a facile hydrothermal route, the BiOCl with higher percentage of {001} facets showed the higher photocatalytic property for degrading methyl orange (MO) [10]. Kim et al. also successfully synthesized ternary nanohybrid composites [11] and graphene-based nanocomposites [12,13] which have demonstrated the wide applications in the environmental issues. Generally speaking, the high density of oxygen atoms on the exposed {001} facet of BiOCI makes the oxygen vacancies more evident [14]. These oxygen vacancies are considered to be relevant to the improved photocatalytic activity. So a higher oxygen vacancy density exhibits higher visible-light photoactivity [9,15].

More recently, AgX (X = Cl, Br and I) photocatalysts [16-18], well known as the photosensitive materials, have been extensively investigated due to their potential practical applications in the photocatalysis. A variety of catalysts were reported to combine with AgX to improve their photocatalytic performance. For instance, AgX/BiOX [19], AgI/BiOI [20-22], Ag@AgI/ZnS [23], AgCl/ZnO [24], AgX/Ag₂CO₃ [25] and AgBr/Ag₂O [26] all displayed significantly



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increased photocatalytic activity in the degradation of organic pollutant after being combined with the AgX. These results may be due to the heterojunction formed between the different semiconductor photocatalysts. The heterojunction can facilitate the separation of photogenerated charges and reduce the distance of separation, finally improve the photocatalytic performance.

In present work, we prepared AgBr/BiOCl composites with exposed {101} facets on BiOCl microspheres and AgBr/BiOCl with high exposed {001} facets on BiOCl nanosheets by using a simple solvothermal method in ethylene glycol (EG) and water system. As expected, AgBr indeed promoted visible-light response and improved the photocatalytic activities of both composites under the visible light irradiation. Furthermore, the AgBr-{001}BiOCl showed higher photocatalytic activity than that of AgBr-{101}BiOCl. Photocurrent experiments were carried out to investigate the charge transfer in the heterojunction and to get a better understanding over the photocatalytic reactions. A possible photocatalytic mechanism of the enhanced AgBr-{001}BiOCl heterojunctions was also proposed according to the experimental results.

2. Experimental section

2.1. Sample preparation

2.1.1. Synthesis of {101} BiOCl and {001} BiOCl

All chemicals were of analytical grade and applied without other purification. BiOCl microspheres with exposed {101} facets were synthesized via a facile solvothermal process. In a typical procedure, 5 mmol Bi(NO₃)₃·5H₂O and 5 mmol KCl were dissolved in 20 mL ethylene glycol (EG) under magnetic stirring, respectively. After 30 min, the KCl solution was slowly added to the $Bi(NO_3)_3 \cdot 5H_2O$ solution drop by drop. Then the mixture was transferred to a 50 mL Teflon-lined stainless steel autoclave after stirring for another 30 min at room temperature. Subsequently, the mixture was carried out at 160 °C for 12 h. The product was collected by centrifugal separation, washed with distilled water and absolute ethanol for several times, then dried at 60 °C overnight. This sample was labelled as {101}BiOCl. And the {001}BiOCl was prepared through a simple hydrothemal method. Similarly, 5 mmol Bi(NO₃)₃·5H₂O and 5 mmol KCl were dispersed into 20 mL deionized water with continually stirring, respectively. Then the latter was dropped to the previous solution after stirring for 30 min. At the same time, 2 mol/L NaOH was added to this suspension to adjust the pH value to 7.0. And other conditions were the same with that of {101} BiOCl. The sample was labelled as {001}BiOCl.

2.1.2. Synthesis of AgBr-{101} BiOCl and AgBr-{001} BiOCl

Taking AgBr-{101}BiOCl (1:1) as an example, 1 mmol AgNO₃ and 1 mmol {101}BiOCl were dispersed equably in 10 mL deionized water in a beaker to form suspension A, and 1 mmol KBr was dissolved in 10 mL distilled water to form solution B at the same time. Then solution B was added into suspension A drop by drop with strongly stirring. The mixture was continuously stirred for 0.5 h. And the AgBr-{101}BiOCl and AgBr-{001}BiOCl composites with different mole ratios of AgBr were successfully achieved in the same way. Finally, the samples were washed with deionized water for three times, collected and dried at 60 °C. The mole ratios of the obtained samples were considered to be AgBr-{101}BiOCl (1:1), AgBr-{101}BiOCl (1:2), AgBr-{101}BiOCl (1:4), AgBr-{001}BiOCl (1:1), AgBr-{001}BiOCl (1:2) and AgBr-{001}BiOCl (1:4).

In comparison, the AgBr photocatalyst was also synthesized. Firstly, 5 mmol AgNO₃ and 5 mmol KBr got dissolved in 10 mL deionized water, respectively. Then the solutions were mixed under magnetic stirring with continuously stirring for 30 min. Finally, the sample was washed, collected and dried at 60 °C.

2.2. Characterization

Thermo ARL SCINTAG X'TRA X-ray diffractometer was used to analyze the X-ray diffraction patterns spectrum of as-prepared samples at room temperature by using Cu K a radiation. The Hitachi S-4700 SEM was used to characterize scanning electron microscope images of the morphologies and structures over samples. Lambda 850 UV-vis spectrophotometer was used to test the UV-vis diffuse reflectance spectra with BaSO₄ as a reference. XPS characterization was collected by performing on a X-ray photoelectron spectroscopy analyzer (KRATOS AXIS ULTRA DLD). The photocurrent experiment was analyzed on a CHI-660C electrochemical work station (Made in China), using a common threeelectrode chemical cell, and 0.1 mol/L Na₂SO₄ agueous liguor works as electrolyte solution. The 0.1 mg of as-prepared sample was coupled on ITO glass that acted as the working electrode. The reference electrode was a saturated Ag-AgCl electrode and the counter was a platinum wire.

2.3. Photocatalytic experiments

In a typical photocatalytic experiment, the RhB and phenol were used to evaluate the photocatalytic performance of the as-prepared samples under visible/solar light irradiation. Firstly, 0.1 g of the photocatalyst was dispersed in 200 mL 2 \times 10⁻⁵ mol/L RhB (or 50 mL 50 mg/L phenol) solution, then the suspension was stirred intensely in darkness for 30 min prior to irradiation toward establishing the adsorption–desorption equilibrium. And during the procedure of photodegradation, 3 mL suspension was collected per 3 min, the concentration of RhB was detected using a UV759S UV–Vis spectrophotometer after centrifuged, and a 300 W Xe lamp with a 420 nm cut off filter worked as the visible-light source.

The degree of RhB mineralization was also measured through the total organic carbon (TOC) in the irradiated solutions at a certain time intervals using a TOC-VCPH analyzer (Shimadzu Co., Japan). A typical photocatalytic experiment system is consisted of 200 mL 2×10^{-5} mol/L RhB solution and 0.1 g of the photocatalyst.

3. Results and discussion

As shown in Fig. 1, the crystallographic structure of the asprepared samples synthesized in water was characterized by XRD. It can be seen that the diffraction peaks of curve *a* and *b* in the XRD patterns are readily indexed to the AgBr (JCPDS card No. 06-0438) and BiOCl (JCPDS card No. 06-0249), respectively. For the BiOCl, the characteristic peaks of (001), (101) and (102) are sharper and stronger. For the AgBr, the peaks at $2\theta = 26.78^{\circ}$, 30.98° , 44.40° and 55.08° were assigned to the (111), (200), (220) and (222) planes, respectively. The XRD patterns of AgBr/BiOCl heterostructured photocatalyst samples with different mole ratios 1:4, 1:2 and 1:1 are shown in Fig. 1 c to e. It is clearly seen that the samples c to *e* have the pure phases of both AgBr and BiOCl. Meanwhile, it is noteworthy that the (200) peak belonging to the AgBr is obviously strengthened as the increased content of AgBr. These observations indicates that the AgBr has been successful grafted onto BiOCl. No other characteristic peaks of impurities can be detected, demonstrating high purities of all samples. And the sharp diffraction peaks suggest that the as-prepared samples are well-crystallized. The intensity ratio of the (001) to (101) peaks for the b to e is 0.91, 0.97, 0.96 and 0.94, respectively. It can be inferred that the BiOCl which prepared in water had high percentage of {001} facets.

Fig. 2 shows the XRD patterns of the samples which prepared in ethylene glycol (EG). The samples ranging from *a* to *e* are AgBr,



Fig. 1. XRD diffraction patterns of the AgBr (a), BiOCl (b) and AgBr/BiOCl samples with different mole ratio of 1:4 (c), 1:2 (d) and 1:1 (e) synthesized in water.

BiOCl and AgBr/BiOCl heterojunctions with different mole ratios of 1:4, 1:2 and 1:1, respectively. Compared to the diffraction peaks in Fig. 1, it can be found that the diffraction peaks intensity of (001) and (101) in Fig. 2 are lower. Meanwhile, the diffraction intensity ratio of (001)/(101) planes for the BiOCl and AgBr/BiOCl heterojunctions prepared in EG are 0.43, 0.48, 0.45 and 0.56. This means that the BiOCl prepared in EG may grow along the (101) plane, suggesting that the as-prepared samples have a high exposure percentage of {101} facets, for which the sample was labelled as {101}BiOCl.

The morphology and structure of the resultant samples were observed by SEM. It is clearly seen that well-defined AgBr particles (see Fig. 3a) are in a small size. Fig. 3b shows that the {101}BiOCl consists of microsphere with diameters about 7 μ m. The AgBr-{101} BiOCl (1:2) heterojunction was also characterized by SEM (Fig. 3c) which indicates that AgBr is well embedded in {101}BiOCl surface.



Fig. 2. XRD diffraction patterns of the AgBr (a), BiOCl (b) and AgBr/BiOCl samples with different mole ratio of 1:4 (c), 1:2 (d) and 1:1 (e) synthesized in EG.

For comparison, the morphology of BiOCl prepared in water was also observed which can be seen from Fig. 3d that the sample was assembled of interlaced nanosheets. And the SEM images of AgBr-{001} BiOCl (1:2) (Fig. 3e) also depict that AgBr are adhered well to the {001}BiOCl. Besides, Fig. 3c and e also exhibit that the morphology of the composites does not change after embedding AgBr particles. Furthermore, XPS was performed to explore the chemical compositions and valence states of as-prepared AgBr-{001}BiOCl (1:2). From the full scan spectrum exhibited in Fig. 3f, the peaks of Bi (4p), O (1s), Bi (4d), Ag (3d), Cl (2p), O (2s) and C (1s) elements can be identified in the heterojunction as a proof of the chemical purity of AgBr-{001}BiOCl (1:2). The C signal primarily derives from the hydrocarbon of XPS instrument itself. As shown the inset in Fig. 3f, the binding energy values of Ag $3d_{3/2}$ and Ag $3d_{5/2}$ 2 are observed at 374.2 eV and 368.5 eV, respectively, which are in good agreement with the values reported for Ag⁺. And no obvious peaks belonging to the Ag⁰ was observed, indicating that the AgBr-{001}BiOCl heterostructures are rather stable.

It is known that the optical absorption property of catalysts is one of the vital factors that determine their photocatalytic properties. Hence, the UV-vis diffuse reflectance spectra of the catalysts with different amounts of AgBr particles are shown in Fig. 4. As showed in Fig. 4a, the pure AgBr shows strong absorption edge at about 478 nm in whole range of visible light region which is in good agreement with the previously reported results [27]. The {101} BiOCl microsphere without AgBr has an absorption wavelength at about 390 nm. As for AgBr-{101}BiOCl (1:1), AgBr-{101}BiOCl (1:2) and AgBr-{101}BiOCl (1:4), the optical absorption edges shift slightly to longer wavelengths, showing an apparent red-shift compared with {101}BiOCl, and this red-shift exhibits inconspicuous change with different content of AgBr. By contrast, {001}BiOCl (Fig. 4b) shows the maximum absorbance at about 360 nm, which seems that the {001}BiOCl possessed the favorable photoabsorption property in the UV light region. The maximum absorbance edges of the AgBr-{001}BiOCl composites with different mole ratio of 1:1, 1:2 and 1:4 are 380, 377 and 375 nm, respectively. Compared to the {001}BiOCl, the existence of the AgBr can increase its photoabsorption with absorption edges shifting to larger wavelengths. The results showed that all samples exhibit strong UV photoabsorption. However, {101}BiOCl and {001}BiOCl displayed quite different light absorption in the visible light region (360-800 nm). Moreover, the {101}BiOCl and the AgBr-{101}BiOCl heterostructures displayed a broader absorption wavelengths from the UV light region to the visible light region than that of {001} BiOCl and the AgBr-{001}BiOCl.

It is proverbial to figure out the band gap energies of AgBr, {001} BiOCl and {101} BiOCl on the basis of the DRS result by using the following equation [28].

$$A(h\nu - Eg)^{n/2} = \alpha h\nu \tag{1}$$

where *a*, *h*, *A*, *v* and *E*_g are adsorption coefficient, Plank constant, proportionality constant, light frequency and band gap, respectively. In the equation, n is decided by the type of optical transition in a semiconductor, where n = 4 for indirect transition and n = 1 for direct transition. Fig. 4c displays the plots of $(\alpha h\nu)^{1/2}$ against h ν for the samples. The band gap energies of AgBr, $\{001\}$ BiOCl and $\{101\}$ BiOCl are calculated to be 2.56, 3.44 and 3.51 eV, respectively. Generally speaking, the optical band gap in crystals is anisotropic and decided by the direction of the crystal [29]. The small difference of Eg values between the $\{001\}$ BiOCl and $\{101\}$ BiOCl samples may be attributed to the difference of the morphology and the percentage of exposed $\{101\}$ facets or $\{001\}$ facets. In addition, the electric potentials of the VB and CB of the samples can be calculated by Mulliken electronegativity theory [30,31]:



Fig. 3. SEM images of AgBr (a), {101}BiOCl (b), AgBr-{101}BiOCl (1:2) (c), {001}BiOCl (d) and AgBr-{001}BiOCl (1:2) (e), together with XPS survey spectra of AgBr-{001}BiOCl (1:2) and Ag 3d (f).

$$E_{CB} = X - E_C - 0.5E_g$$
 (2)

$$E_{VB} = E_{CB} + E_g \tag{3}$$

where *Eg* and *X* are the band gap energy and the electronegativity of semiconductor, respectively. E_{CB} is the conduction band and E_{VB} is the valence band edge potentials, respectively. *Ec* is the energy of free electrons about 4.5 eV on the hydrogen scale. The values of *X* for AgBr and BiOCl are 5.81 and 6.36 respectively. Therefore, the E_{CB} and E_{VB} of AgBr are calculated to be 0.03 eV and 2.59 eV. Through potential calculation, it is found that the conduction band of {101} BiOCl is located at 0.11 eV, which is more negative than that of {001} BiOCl (0.14 eV). Meanwhile, the valence band of {101}BiOCl is 3.62 eV, which is more positive than the VB potential of {001}BiOCl (3.58 eV).

The photocatalytic activity of all samples was evaluated by photodegrading RhB under visible light. All the samples are firstly disposed for 0.5 h without light irradiation to achieve an adsorption-desorption equilibrium. Fig. 5a displays the variation of RhB concentration (C/C_0) versus the irradiation time of AgBr-{101} BiOCl (1:1), AgBr-{101}BiOCl (1:2), AgBr-{101}BiOCl (1:4) and AgBr, respectively. AgBr-{101}BiOCl (1:2) shows a relatively better photocatalytic activity, with a degradation ratio of 87.9% after 15 min. Obviously, different facets of AgBr/BiOCl composites have different photocatalytic activity for the photodegradation of RhB under the visible light irradiation. For comparison, Fig. 5b shows the photodegration abilities of {001}BiOCl and their heterojunctions. The concentration of RhB decrease rapidly in the presence of the AgBr-{001}BiOCl (1:2) samples, which shows the highest photocatalytic activity. For pure BiOCl sample and AgBr, the total degradation of RhB can only reach 84.4% and 57.9% after 15 min of visible light irradiation. Besides, the physical mixture of {001}BiOCl and AgBr photocatalysts show lower photocatalytic activity than the AgBr-{001}BiOCl (1:2) heterojunction. As for the heterojunctions fabricated by BiOCl and AgBr, they all showed better photocatalytic performance than that of pure AgBr or BiOCl.

The kinetics of RhB photodegradation was calculated



Fig. 4. Diffuse reflectance spectra of the samples prepared in EG (a) and water (b); (c) Plots of $(ah\nu)^{1/2}$ versus $h\nu$ for the AgBr, {001}BiOCl and {101}BiOCl.

quantitatively by fitting the experimental data with the pseudo-first-order model [32,33], as expressed by



Fig. 5. Photodegradation efficiencies of RhB over the samples prepared in EG (a) and water (b).

$$\ln(C/C_0) = kt \tag{4}$$

where k is the apparent first-order rate constant, t, C and C₀ are the degradation time, concentration and initial concentration of RhB during the photodegradation reaction, respectively. Table 1 exhibits the photodegradation rate constants over different catalysts. The rate constants for the degradation of RhB over the {101}BiOCl, AgBr-{101}BiOCl (1:1), AgBr-{101}BiOCl (1:2) and AgBr-{101}BiOCl (1:4) are 0.0663, 0.0818, 0.1368 and 0.1341 min⁻¹, respectively. While the photocatalytic degradation constants of {001}BiOCl, AgBr-{001}BiOCl (1:1), AgBr-{001}BiOCl (1:2) and AgBr-{001}BiOCl (1:4) are

The photocatalytic degradation rate constant of RhB in the presence of samples.	Table 1	
	The photocatalytic degradation rate constant	of RhB in the presence of samples.

Photocatalyst	$k/(\min^{-1})$	Photocatalyst	$k/(\min^{-1})$
AgBr	0.0573	AgBr	0.0573
AgBr-{101}BiOCl (1:1)	0.0818	AgBr-{001}BiOCl (1:1)	0.1236
AgBr-{101}BiOCl (1:2)	0.1368	AgBr-{001}BiOCl (1:2)	0.2533
AgBr-{101}BiOCl (1:4)	0.1341	AgBr-{001}BiOCl (1:4)	0.1308
{101}BiOCl	0.0663	{001}BiOCl	0.1223

calculated to be 0.1223, 0.1236, 0.2533 and 0.1308 min⁻¹, respectively. And the rate constant for AgBr is 0.0573 min⁻¹. It is obvious that photocatalytic activity of all the AgBr-{001}BiOCl composites is higher than that of the AgBr-{101}BiOCl. Besides, the photocatalytic activity of the AgBr-{001}BiOCl (1:2) composites is approximately 2 times of the AgBr-{101}BiOCl (1:2). It can be seen from the results that AgBr-{001}BiOCl (1:2) possesses the best photocatalytic activity under visible light irradiation, which may be due to synergetic effect of the higher percentage of exposed {001} facetson the catalyst's surface and the photosensitization of AgBr.

To investigate the mineralization of organic compounds on the AgBr-{001}BiOCl (1:2) composites, the Total Organic Carbon (TOC) analysis was carried out to determine the mineralization of RhB during the photocatalytic reaction (Fig. 6). As can be seen that the TOC removal increases with the irradiation time and arrives at 21.48% through consecutive irradiation of visible light within 15 min (Fig. 6). The degree of mineralization reached 98% for RhB after 210 min of visible light irradiation. The results demonstrate that not only the chromophoric group but also the aromatic groups in the RhB molecules are attacked in the photocatalytic reaction. In addition, these results also indicate that the completely destruction of RhB is possible. In this experiment, the AgBr-{001}BiOCl (1:2) composite with the highest photocatalytic activity was also used to evaluate the photocatalytic degradation of phenol in order to rule out the photosensitization effect under light irradiation. As shown in Fig. 7, the phenol degradation efficiency is nearly 100% when the AgBr-{001}BiOCl (1:2) composite was irradiated for 150 min which indicates that the AgBr-{001}BiOCl (1:2) composites also exhibit superior activities for phenol degradation.

In addition, the reusability and stability of a photocatalyst is a significant parameter for practical applications. So in order to evaluate the reusability and stability of the AgBr-{001}BiOCl (1:2) samples during photocatalytic degradation process, a recycling test of the degradation of RhB was carried out, and the experimental results are shown in Fig. 8. After each run of repetitive photocatalysis reactions, all of the photocatalysts were collected and centrifuged for the next recycling test. A slight decrease in photodegradation of RhB, which is attributed to the loss of catalysts during the decontamination. Recycling test shows that the AgBr-{001}BiOCl (1:2) photocatalysts possess relatively good stability. For the purpose of investigating the structural stability of the AgBr-



Fig. 6. The TOC evolution as a function of irradiation time in AgBr-{001}BiOCI (1:2) photocatalysis process.



Fig. 7. The UV–Vis absorption spectra of phenol under solar light irradiation using AgBr-{001}BiOCl (1:2) as photocatalyst.



Fig. 8. The cycling stability of AgBr-{001}BiOCl (1:2) photocatalyst for degradation of RhB under visible light irradiation.

{001}BiOCl (1:2) photocatalyst after three recycling measurements, the catalyst was centrifuged and washed with distilled water for several times, collected and dried at 60 °C overnight. Fig. 9 shows XRD patterns of AgBr-{001}BiOCl (1:2) after three recycling measurements. It can be seen that there exhibit similar diffraction peaks in Fig. 9 compared with Fig. 1d, suggesting similar crystal structures. Not only the diffraction peaks of AgBr but also the diffraction peaks of BiOCl can be observed in the XRD patterns. In particular, the (200) and (220) diffraction peaks in the XRD patterns belonging to the AgBr can be observed. No any impurity can be detected, which indicates that the structure of AgBr-{001}BiOCl (1:2) photocatalyst is relatively stable.

As is know that the photocurrent experiment is related to the transfer of the photo-generated electrons and holes, therefore, it can represent the separation and recombination of the photo-generated carriers. The transient photocurrent responses of the samples were also recorded under simulated visible light irradiation under the light-on and light-off cycles. In Fig. 10a, the photo-electrode of the AgBr-{101}BiOCl (1:2) shows the highest photocurrent density compared with the AgBr and {101}BiOCl



Fig. 9. XRD diffraction patterns of AgBr- $\{001\}$ BiOCl (1:2) samples after three recycling measurements.



Fig. 10. Photocurrent response for pure AgBr, AgBr-{101}BiOCI (1:2) and {101}BiOCI (a); AgBr, AgBr-{001}BiOCI (1:2) and {001}BiOCI (b) under visible light irradiation.

photoelectrodes, indicating the efficient separation of photoinduced charges and the faster transfer of charges in the AgBr-{101}BiOCl (1:2) composite. It is commonly believed that the higher photocurrent density leads to a higher charge separation efficiency, resulting in higher catalytic performance. Similarly, the AgBr-{001} BiOCl (1:2) heterojunction also displays the highest photocurrent intensity than AgBr and {001}BiOCl as shown in Fig. 10b. It is clearly that the AgBr-{001}BiOCl (1:2) shows the better photocatalytic activity than that of AgBr-{101}BiOCl (1:2) according to the experiment result (Fig. 5a and b), which may indicate that the BiOCl sheets with high percentage of {001} facets exposed are beneficial to the photocatalytic activity. As is known that Bi and O atoms are normally arranged orderly in the (001) facet of the BiOCl, this means that more oxygen atoms are exposed. Therefore, the oxygen vacancies can be formed easily on the surface of BiOCl, coming from the low chemical bonding energy of Bi-O [34]. Moreover, under the irradiation, disorder of the BiOCl surface might be caused since the energy is very powerful [35]. As a result, the length of Bi-O bonds is increased and the Bi-O bond can be considered broken to a certain degree. This particularly facilitates the release of O atoms which come from the surface of BiOCl, and then the oxygen vacancies can be generated [10]. Oxygen vacancy is always considered as one kind of point defect which plays an important role in the photocatalytic activity for the degradation of RhB. It has been reported that the oxygen vacancy in BiOCl can extend the photoabsorption of BiOCl to visible-light region and facilitate the separation efficiency of photogenerated electrons and holes [2], subsequently enhance the photocatalytic performance. Therefore, the tremendous enhancement of photocatalytic activity on AgBr-{001}BiOCl are mainly attributed to the synergy between the high {001} exposed and defects (oxygen vacancy).

To further identify the photocatalytic mechanism, different scavengers were introduced to evaluate the contributions of active species on the photodegradation, the results are shown in Fig. 11. The system was added 2 mg benzoquinone (BQ), 2.13 mg ammonium oxalate and 15 mL isopropanol (IPA) which act as superoxide radicals ($\bullet O_2^-$) scavenger, holes (h⁺) scavenger and hydroxyl radicals ($\bullet OH$) scavenger, respectively. As shown in Fig. 11, benzoquinone suppresses the degradation of RhB, indicating that superoxide radicals play an important role in the photodegradation reaction. It is well known that the isopropanol is a quencher of $\bullet OH$, the photodegradation rate does not decreased obviously when isopropanol



Fig. 11. Effects of radical scavengers in the degradation process of RhB over the AgBr-{001}BiOCl (1:2) heterojunction.



Fig. 12. Schematic illustration of the AgBr-{001}BiOCl (1:2) photocatalytic reaction process under visible-light irradiation.

was added, suggesting that •OH radical has negative effect in the photocatalytic process. Furthermore, the addition of ammonium oxalate decreased the degradation rate of RhB, demonstrating the participation of holes (h^+) in the photocatalytic reaction. Above results demonstrate that the h^+ and $\cdot O_2^-$ are the major active species in the photocatalytic degradation reaction on AgBr-{001}BiOCl (1:2) heterojunction under visible light irradiation.

According to the above experiment results, a schematic illustration for highly proposed band gap structures of the AgBr-{001} BiOCl (1:2) heterojunctions is shown in Fig. 12. The redox potentials of valence band (VB) and conduction band (CB) of BiOCl are more positive than those of AgBr, so there is an interactive structure formed by BiOCl and AgBr, which is favorable for the effective separation of photo-induced charge carriers. Under visible light irradiation, the band gap of AgBr is relatively narrow, and the electrons in valence band can be excited to the conduction band of AgBr. Then the photogenerated electrons can transfer from the CB of AgBr to that of BiOCl. The photogenerated electrons in the CB of BiOCl can react with O_2 to yield O^{2-} radicals, which may react with organic molecules (RhB) to make them degradable. In addition, the electrons in oxygen vacancies will reduce the molecular oxygen that are absorbed on the surface of AgBr-{001}BiOCl composites to produce $\cdot O_2^-$ radicals, then the photocatalytic degradation reactions process can be carried on successfully. Therefore, the treated composites with oxygen vacancies show the higher visible light photocatalytic activity. Meanwhile, the h⁺ in the VB of BiOCl can transfer to that of AgBr, since the VB potential of AgBr is more negative than that of BiOCl. In this way, the photogenerated electron-hole pairs on AgBr-{001}BiOCl composites can be effectively separated, eventually leading to the higher photocatalytic activity.

4. Conclusion

In summary, a series of AgBr/BiOCl composites with different facets were successfully synthesized through a solvothermal and chemical precipitation method by hybridizing BiOCl with AgBr. The as-prepared AgBr-{001}BiOCl composites with high exposed {001} facets exhibit higher photocatalytic activity than that of AgBr-{101} BiOCl microspheres towards degradation of RhB under visible light irradiation. Oxygen vacancies are formed in situ on the exposed {001} facets of BiOCl, which can significantly enhance the light absorption and boost the interfacial charge transfer in the visible-

light region. The oxygen vacancies plays a positive role in the dye degradation processes. The synergetic effect of the highly exposed crystal facets and photosensitization of AgBr can improve the photocatalytic performance of AgBr-{001}BiOCl composites and facilitate its practical applications in the environmental protection issues in future.

Compliance with ethical standard

Conflict of interest the authors declare that they have no conflict of interest.

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