Photocatalytic performance of Ag$_3$PO$_4$/BiOBr heterojunctions induced by effective interfacial charge separation

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Abstract

In this work, Ag$_3$PO$_4$/BiOBr heterojunction photocatalyst was prepared by a precipitation method. The formation of Ag$_3$PO$_4$/BiOBr heterojunctions was proven by X-ray diffraction, energy-dispersive X-ray spectroscopy and high-resolution transmission electron microscopy. The as-prepared samples were characterized by scanning electron microscopy, UV-Vis diffuse reflectance spectrum and Brunauer–Emmett–Teller surface area. Separation behaviors of photoinduced carriers were investigated by surface photovoltage spectroscopy, the results display that the separation rate of photoinduced carriers of Ag$_3$PO$_4$/BiOBr heterojunctions was significantly promoted. The activities of the photocatalysts were evaluated by destruction of Rhodamine B (RhB) and methyl orange (MO). The results exhibit that the photocatalytic performance of Ag$_3$PO$_4$/BiOBr photocatalyst is higher than that of the reference BiOBr. The degradation rate constant of RhB and MO over Ag$_3$PO$_4$/BiOBr is about 3 and 2.8 times of that on the reference BiOBr under visible light irradiation, respectively, which can be attributed to the significantly promoted light response capacity to visible light and enhanced separation efficiency of photo-generated carriers of BiOBr originated from the coupling of Ag$_3$PO$_4$ and BiOBr. In view of the observations, photocatalytic enhancement mechanism of Ag$_3$PO$_4$/BiOBr was proposed.

Keywords: Heterojunctions; Ag$_3$PO$_4$/BiOBr; Semiconductors; Charge separation

1. Introduction

Nowadays, with the rapid development of industrial technology and the social economy, a large number of toxic organic pollutants are directly discharged into the atmosphere, water, and soil, which becomes a serious threat to human life and social-economic development [1,2]. For instance, Rhodamine B (RhB) and methyl orange (MO) are two typical organic dyes, which may form serious menaces to human health and ecosystem since they have been widely used in various industries and their carcinogenic and deformity [3]. Recently, photocatalysis has attracted widespread attention due to its ability to directly utilize solar energy for energy conversion and environmental purification [4,5]. Therefore, it is of great significance to seek highly active photocatalysts with broad-spectrum absorption efficiency, rapid carrier transfer efficiency, long-term stability, and lifetime [6,7].

As a novel visible-light driven photocatalyst, BiOBr has received increasing attention due to its excellent chemical stability, suitable band gap and special hierarchical structure [8–14]. However, because of its low light quantum efficiency, the photocatalytic activity of BiOBr is still low, which greatly restricts its practical applications. According to previous reports [15–21], the heterojunctions constructed by BiOBr and other semiconductor materials.
exhibit excellent photocatalytic activity, such as Fe₃O₄/BiOBr [22], BiOBr/BiOIO₃ [23], BiVO/BiOBr [24] and so on. Among the existed photocatalysts, Ag₃PO₄ is an ideal candidate to couple with BiOBr [25,26]. Bandgap of Ag₃PO₄ is 2.4 eV, and the corresponding absorption threshold is about 525 nm [27,28], which can well absorb visible light. In addition, Ag₃PO₄ has relatively high oxidation ability and can effectively degrade organic pollutant molecules under visible light irradiation. It has been reported that a graphene wrap BiOBr/Ag₃PO₄ Z-scheme heterojunction was successively synthesized by solvothermal and precipitation method. The as-obtained BiOBr/Ag₃PO₄/rGO composite presents excellent photocatalytic activity and mineralization ability for TC degradation. The stack disorder which cased by the intercalation of BiOBr and Ag₃PO₄ into two-dimensional stacked rGO thin layers is beneficial for increasing photocatalytic activity. But in fact, BiOBr/Ag₃PO₄ also performed higher photocatalytic performance than BiOBr in this report, which is nearly 2.2-folds of that of the reference BiOBr [29]. Besides, separation behaviors of photoinduced carriers haven’t been investigated by surface photovoltage spectroscopy (SPS).

Herein, in this work, Ag₃PO₄/BiOBr composite photocatalyst was in-situ prepared by a precipitation approach [30–34]. Using RhB and MO as model pollutants, photocatalytic activity and stability of the catalyst were investigated. The interfacial charge separation behavior of the Ag₃PO₄/BiOBr composite was thoroughly investigated. The promoted photocatalytic performance of Ag₃PO₄/BiOBr can be allocated to the effective separation of photoinduced carriers.

2. Experimental section

2.1. Preparation of BiOBr

BiOBr nanosheets were synthesized via a hydrothermal method. 0.01 mol Bi(NO₃)₃∙5H₂O was added into 40 mL glacial acetic acid, and solution A was obtained by ultrasonification for 10 min. 0.01 mol KBr was added into 20 mL deionized water and stirred for 5 min to obtain solution B. Solution B was slowly added to solution A dropwise and continued to stir for 30 min. The resulting milky suspension was then transferred to a 100 mL polytetrafluoroethylene reactor for microwave hydrothermal reaction at 180°C for 2 h. After cooling to room temperature, the obtained product was washed with deionized water and anhydrous ethanol for three times, respectively, and then was dried in an oven at 60°C for 24 h to obtain BiOBr.

2.2. Preparation of Ag₃PO₄/BiOBr heterojunctions

Ag₃PO₄/BiOBr heterojunctions were synthesized in-situ via a precipitation method. 1.0065 g BiOBr was dispersed into 40 mL deionized water, and the suspension solution was obtained by sonication for 30 min. Then, 0.1700 g AgNO₃ was added into the suspension in dark. After stirring for 30 min, 10 mL Na₃PO₄ solution containing 0.1267 g Na₃PO₄·12H₂O was added dropwise to the above suspension and was continuously stirred at room temperature for 4 h. After filtration, the product was washed with deionized water and absolute ethanol for three times, respectively, and then was dried in an oven at 60°C for 24 h to obtain Ag₃PO₄/BiOBr heterojunctions. To ensure consistent experimental conditions, Ag₃PO₄ was obtained according to the above steps without adding of BiOBr.

2.3. Evaluation of photocatalytic activity

In this work, the performance of photocatalysts was measured by destruction of simulated organic pollutants in sewage using a Xe lamp (PLS-SXE 300C 300 W) with a cut-off filter (λ > 420 nm) to remove ultraviolet light. The simulated sewage was RhB and MO aqueous solution (10 mg/L). 0.05 g the prepared catalyst was put into 50 mL RhB or MO aqueous solution, respectively. The mixture containing quantitative sample and RhB or MO was stirred for 30 min in dark to acquire an adsorption–desorption equilibrium. To monitor the concentration of pollutants, after a specific irradiation interval, 5 mL suspension was taken out and the powder was moved from the suspension solution by high-speed centrifugation. A 756 PC spectrophotometer was used to determine the absorbance of RhB and MO solution at 554 and 464 nm, respectively.

3. Results and discussion

3.1. Characterization of the samples

To investigate the effect of construction of heterojunction on the specific surface area Brunauer–Emmett–Teller of the catalyst, the S BET of samples was detected and is presented in Table 1. The specific surface area of Ag₃PO₄/BiOBr heterojunctions is higher than that of BiOBr. The enhancement in specific surface area is probably due to the existence of Ag₃PO₄ on the surface of BiOBr. Commonly, high specific surface area is favorable for the photocatalytic activity.

Fig. 1 shows the X-ray diffraction (XRD) patterns of BiOBr, Ag₃PO₄ and Ag₃PO₄/BiOBr heterojunctions. It can be seen that all the diffraction peaks of the pure BiOBr and Ag₃PO₄ correspond to the standard BiOBr XRD card (JCPDS No.09-0393) and the standard Ag₃PO₄ XRD card (JCPDS No.06-0505). In addition, for Ag₃PO₄/BiOBr heterojunctions, the diffraction peaks of BiOBr and Ag₃PO₄ can be observed simultaneously, indicating that Ag₃PO₄ and BiOBr have successfully combined. In order to further investigate the microstructure of the prepared samples, scanning electron microscopy (SEM) and high-resolution transmission electron microscopy (HRTEM) measurements were carried out.

From Fig. 2a it can be found that BiOBr is nanosheets (about 1–2 µm) with a smooth surface. In Fig. 2b many irregular Ag₃PO₄ nanoparticles were successfully deposited on the surface of BiOBr. Energy-dispersive X-ray (EDS) spectrum of Ag₃PO₄/BiOBr is shown in Fig. 2c. It is apparent that the characteristic peaks for elements such as Ag, O, Bi and Br appear in the spectrum, further indicating that Ag₃PO₄ and BiOBr coexist in the heterojunctions. From

<table>
<thead>
<tr>
<th>Sample</th>
<th>BiOBr</th>
<th>Ag₃PO₄/BiOBr</th>
</tr>
</thead>
<tbody>
<tr>
<td>S BET (m²/g)</td>
<td>3.8</td>
<td>4.0</td>
</tr>
</tbody>
</table>
the HRTEM of the Ag₃PO₄/BiOBr sample demonstrated in Fig. 2d, the lattice spacing of 0.2138 nm and 0.1984 nm corresponds to the (220) crystal plane of the cubic phase Ag₃PO₄ and the (200) crystal plane of the tetragonal phase BiOBr, respectively. The HRTEM result is in good agreement with the results obtained by XRD, SEM, and EDS. These results prove that Ag₃PO₄ was successfully loaded on the surface of BiOBr.

Fig. 3a is the UV-Vis diffuse reflectance spectrum (UV-Vis DRS) spectra of the sample. It can be seen that the absorption threshold of the pristine BiOBr is about 450 nm, which is consistent with previous reports [15]. Compared with BiOBr, the visible light absorption capacity of Ag₃PO₄/BiOBr heterojunction is significantly enhanced, indicating that the existence of Ag₃PO₄ expands the light response range of the catalytic material to visible light, which is beneficial to the improvement of photocatalytic performance. The bandgap of the semiconductor can be calculated by the following formula:

\[
\left( \alpha h v \right)^{1/2} = A (h v - E_g) 
\]

where \(\alpha\) is the absorption coefficient, \(h\) is Planck’s constant, \(v\) is the light frequency, \(A\) is a constant [35] and \(n\) is an index that depends on the electronic transition of the semiconductor [36] (\(n = 1\) for direct-gap semiconductor, \(n = 4\) for indirect-gap semiconductor [23]). For Ag₃PO₄ and BiOBr, the \(n\) value represents 1 and 4, respectively. As shown in Fig. 3b, the bandgap (\(E_g\)) for BiOBr and Ag₃PO₄ is estimated to be 2.63 and 2.16 eV by plotting \((\alpha h v)^{1/2}\) and \((\alpha h v)^{2}\) vs. \(h v\), respectively, which is close to the previous report [29].

Fig. 4a shows the SPS spectra of BiOBr and Ag₃PO₄/BiOBr composite photocatalyst. It can be seen from Fig. 4a that the original BiOBr only responds to light in the range
After coupling with Ag$_3$PO$_4$, light response range of the heterojunctions has significantly expanded to about 500 nm, indicating that the Ag$_3$PO$_4$/BiOBr composite has a stronger visible-light absorption capacity than the single BiOBr, which is consistent with the results obtained by UV-Vis DRS. According to the detection principle of SPS experiment, the intensity of SPS signal corresponds to the separation rate of photocarriers [37]. In addition, the prepared Ag$_3$PO$_4$/BiOBr composite photocatalyst exhibits a stronger SPS signal than BiOBr. BiOBr shows SPS response from 300–400 nm, however, Ag$_3$PO$_4$/BiOBr composite displays strong SPS signal from 300–500 nm, it is evident that the strong and boosted SPS signals of Ag$_3$PO$_4$/BiOBr stems from the presence of Ag$_3$PO$_4$ in the composite. Coupling Ag$_3$PO$_4$ with BiOBr can establish an interfacial electric field due to the different Fermi levels and work functions of two photocatalysts, facilitating the separation of photoinduced carriers. Generally, high separation efficiency of photoinduced carriers is favorable for the photocatalytic performance.

To ascertain the role of the active free radicals, trapping experiments were executed. Benzoquinone (BQ) was selected as the •O$_2$– trapping agent, isopropanol (IPA) as the •OH trapping agent, and ammonium oxalate (AO) as h$^+$ trapping agent. The experimental results were shown in Fig. 4b. It can be observed that addition of benzoquinone has no significant effect on the catalytic activity of the Ag$_3$PO$_4$/BiOBr photocatalyst. Addition of ammonium oxalate and isopropanol significantly inhibits the degradation of RhB over the catalyst, indicating that h$^+$ and •OH are the main active species in the photocatalytic reaction process.

3.2. Photocatalytic performance

Photocatalytic activity of the photocatalysts is shown in Fig. 5a and b. After coupling BiOBr with Ag$_3$PO$_4$, photocatalytic performance of Ag$_3$PO$_4$/BiOBr heterojunction photocatalyst has been significantly improved under visible light irradiation. The results in Fig. 5c and d further show that the degradation rate constant of RhB and MO over Ag$_3$PO$_4$/BiOBr is about 3 and 3.5 times of that on the pristine BiOBr, respectively. From the obtained results, it is apparent that construction of heterojunctions can expand the utilization range of BiOBr for visible light and significantly increase the efficiency of photo-generated electron–hole separation, thereby significantly enhancing its photocatalytic performance.

Fig. 6 presents the stability test results of the Ag$_3$PO$_4$/BiOBr catalyst. After 4 repeated experiments, the degradation efficiency of RhB over the catalyst samples is 90.17%, 85.25%, 78.38% and 72.89%, respectively. After four cyclic
experiments, the catalytic efficiency decreases by about 20%. This may be due to the fall of Ag₃PO₄ from the BiOBr surface during the experiment, which reduces the photocatalytic performance of the sample.

3.3. Photocatalytic mechanism

To explore the photocatalytic mechanism, the relative position of the valance band (VB) and conduction band (CB) of BiOBr and Ag₃PO₄ were estimated by Mulliken electronegativity formula as follows:

Fig. 5. Photocatalytic activities of BiOBr and Ag₃PO₄/BiOBr heterostructures toward degradation of (a) Rhodamine B and (b) methyl orange under visible light irradiation; Fitted first-order kinetic for Rhodamine B (c) and methyl orange (d).

Fig. 6. Stability of the Ag₃PO₄/BiOBr photocatalyst under the visible-light irradiation.

Fig. 7. Photocatalytic mechanism of Ag₃PO₄/BiOBr heterojunctions.
$$E_{\text{VB}} = X - E_g + 0.5E_g$$  (2)
$$E_{\text{CB}} = E_g - E_g$$  (3)

where $E_{\text{VB}}$ and $E_{\text{CB}}$ is the potential valance band and conduction band, respectively. $X$ is the absolute electronegativity of the semiconductor, $E_g$ is the energy of free electrons on the hydrogen scale (about 4.5 eV). The value of $X$ for BiOBr and Ag$_3$PO$_4$ is 6.45 and 5.96 eV [28,38], respectively. Therefore, the $E_{\text{VB}}$ and $E_{\text{CB}}$ for BiOBr is evaluated to be 3.27 and 0.64 eV, respectively, the $E_{\text{VB}}$ and $E_{\text{CB}}$ of Ag$_3$PO$_4$ is calculated to be 2.54 and 0.38 eV, respectively.

In light of the above characterizations and photocatalytic performance assessment results, it is distinct that construction of BiOBr/Ag$_3$PO$_4$ heterostructures can promote the separation of photo-induced charge pairs. The photocatalytic mechanism for Ag$_3$PO$_4$/BiOBr heterojunctions is presented in Fig. 7. Ag$^+$_ from Ag$_3$PO$_4$ under light irradiation can promote the separation of e$^-$/h$^+$ pairs and improve photocatalytic activity of the materials due to the surface plasmon resonance effect (SPR). Metal SPR can expedite the separation of photoexcited carriers, which can propagate along the metal surface [39]. Therefore, it is anticipated that ternary Ag/Ag$_3$PO$_4$/BiOBr heterojunctions will display higher photocatalytic activity than the reference BiOBr. The electrons from Ag$^+_n$ nanoparticles can react with $O_2$ to generate $•OH$ radicals ([40]). The photogenerated holes from BiOBr can oxidize H$_2$O/OH$^-$ to form $•OH$ radicals. However, the photogenerated holes of Ag$_3$PO$_4$ only can oxidize OH$^-$ radicals (E($\text{OH}/\text{H}_2\text{O}$)) is 1.99 eV vs. NHE and $E(\text{OH}/\text{H}_2\text{O})$ is 2.68 eV vs. NHE [41,42]. $•OH$ can participate in the photocatalytic degradation of RhB and MO. Therefore, the as-prepared Ag$_3$PO$_4$/BiOBr heterojunctions follow double S-scheme mechanism, which can markedly boost the separation and transfer of photo-generated electrons and holes.

4. Conclusions

In summary, Ag$_3$PO$_4$/BiOBr heterojunctions were in-situ synthesized by a precipitation method. Combination of Ag$_3$PO$_4$ and BiOBr can significantly expand light response range. The interfacial electric field between two semiconductors can effectively improve the photo-generated electron-hole separation efficiency. Under visible light irradiation, Ag$_3$PO$_4$/BiOBr exhibits higher activity than BiOBr, which is nearly 3-fold of that of the reference BiOBr. The separation and transfer of photoinduced carriers follow S-scheme mechanism. This study offers a highly efficient photocatalyst for environmental purification.

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