1 Introduction

Bismuth oxyhalides (BiOX), in which X is a halogen element, is a layered compound having an open, layered crystal structure consisting of positive [BiO₂⁻] layers sandwiched between two slabs of negative halogen ions. These unique layered structures make BiOX exhibit good adsorption properties and excellent photocatalytic activities in waste water and indoor air purification. Among the BiOX family, BiOI is found to be a promising photocatalyst for the removal of organic pollutants under visible light irradiation since BiOI possesses the smallest band gap (1.73–1.92 eV) and strong absorption. However, pure BiOI is always poor in photocatalytic activity because of the rapid recombination of photoinduced electron–hole pairs. It is important to facilitate the separation of electron–hole pairs and thus improve the photocatalytic activities of BiOI. Development of a highly efficient visible light response of BiOI based catalysts to meet the requirement of practical application still remains a challenge.

It is well known that semiconductor combination is an efficient way for the separation of photoinduced carries, and thus raises the photocatalytic efficiency since a heterojunction structure may be formed between different semiconductors. This heterostructure composite photocatalyst results in an efficient charge separation at the interface. Several heterostructures based on BiOI have been reported which showed higher photocatalytic activity than pure BiOI, such as BiOI/WO₃, BiOI/AgI, BiOI/Ag, BiOI/AgI, and BiOI/MoS₂/MoS₂. MoS₂ has a sandwich interlayer structure composed of three stacked atom layers (S–Mo–S) which are bonded together by weak van der Waals forces. The monolayer MoS₂ has been successfully synthesized, and get particular attention in photovoltaic application due to its distinctive electronic, optical, large surface area and catalytically active sites.

In view of the fact that MoS₂ and BiOI are similar in structure, it is envisaged that a BiOI/MoS₂ composite can have the merits of MoS₂ and BiOI, consequently showing high photocatalytic activity under visible light. However, seldom research has been reported on BiOI/MoS₂ composite photocatalytic performance until now. Recently, 2D structure BiOI/MoS₂ (ref. 34) and 3D hierarchical BiOI/MoS₂/AgI were reported which exhibited good photocatalytic activity towards rhodamine B degradation. The degradation efficiencies of RhB after 50 min were 20%, 40% and 96% by 3D hierarchical BiOI, BiOI/AgI and MoS₂/BiOI/AgI under simulated solar irradiation, respectively. However, the photocatalytic activity of 3D hierarchical BiOI/MoS₂ under visible light irradiation has not been reported yet. Therefore, 3D hierarchical BiOI/MoS₂ composite was fabricated by a simple solvent thermal process in this work, and the results show that the as-prepared BiOI/MoS₂ composites exhibited excellent photocatalytic activity for the degradation of methyl orange (MO) in visible light irradiation. The possible photocatalytic mechanism of BiOI/MoS₂ heterostructure to MO degradation is proposed by adding radical scavengers in the photocatalytic system.
2 Experimental methods

2.1 Synthesis of MoS2, BiOI and BiOI–MoS2 composites

All chemical reagents were of analytical grade and used without further purification in this study. For the preparation of MoS2, 5 mmol Na2MoO4 and 20 mmol CS(NH2)2 were dissolved in deionized water with vigorous stirring for 1 h at room temperature. Then, the mixture was transferred into a 100 ml Teflon-lined stainless-steel autoclave. The autoclave was kept at 483 K for 24 h. The sample was obtained by filtration, washed with deionized water and absolute ethanol many times, and then dispersed into absolute ethanol and dried for 12 h at 323 K.

BiOI/MoS2 composite were synthesized by an ethylene glycol (EG)-assisted solvothermal method. In a typical synthesis procedure, 2 mmol Bi(NO3)3·5H2O and 2 mmol KI was dissolved in 15 ml ethylene glycol under ultrasonication for 20 min respectively. Then, the two solutions were mixed and some MoS2 was added to the mixture. The mixture was under vigorous stirring for 15 min, then it was transferred into a 100 ml Teflon-lined stainless-steel autoclave. The autoclave was kept at 433 K for 12 h. The resultant precipitates were collected, repeatedly washed with deionized water and ethanol, and dried for 12 h at 333 K. BiOI/MoS2 composites were named as BiOI–(wt% of MoS2)MoS2. For comparison, BiOI was also fabricated as the same method without the presence of MoS2.

2.2 Characterization

The morphologies of the prepared BiOI, MoS2 and BiOI–(0.5%) MoS2 samples were characterized by a PANalytical B.V. MPD2094 X-ray diffractometer (XRD) with Cu Kα radiation (λ = 1.5406 Å). Scanning electron microscopy (SEM) pictures and quantitative standard microanalyses were obtained using an energy dispersive X-ray analysis (EDS) with a Zeiss ultra plus FESEM apparatus. UV-vis diffuse reflectance spectrum (DRS) was recorded on a Perkin Elmer Lambda 35 UV-vis spectrophotometer with BaSO4 as a reference, and the scanned range being 200–800 nm against barium sulfate standard. N2 adsorption–desorption isotherm was conducted on a Micromeritics ASAP-2020-HD88 volumetric gas sorption apparatus using 99.999% pure N2.

The photoluminescence (PL) measurements were performed on a Hitachi F7000 Fluorescence Spectrophotometer with an excitation wavelength of 325 nm at room temperature. The photocurrents were performed in 0.5 mol l−1 Na2SO4 solution using an electrochemistry workstation (CHI 660, China) with a three-electrode system. The obtained sample was served as the working electrode (1 mg of the as-prepared sample was dispersed in 0.2 ml of ethanol and 0.2 ml of ethanol mixture to produce a suspension, which was then dip-coated onto an ITO glass electrode). A platinum plate and a saturated Ag/AgCl were used as the counter electrode and reference electrode, respectively. A 300 W Xe lamp with main emission wavelength 420 nm in the range of 420–780 nm along with a power of 80 mW cm−2 was utilized as the photosource.

2.3 Photocatalytic activity tests

The photocatalytic activity tests of the obtained samples were investigated by evaluating in terms of the degradation of methyl orange (MO) solution under the simulated sunlight irradiation. The photochemical reactor contains 40 mg catalysts and 5.0 × 10−3 mol l−1 of 100 ml MO. A 300 W Xe lamp with main emission wavelength 420 nm in the range of 420–780 nm along with a power of 20 mW cm−2 (Beijing Science and Technology Co., Ltd. Park Philae), was set inside a cylindrical reactor, and surrounded by a circulating water jacket to cool the lamp and minimize infrared radiation. The methyl orange aqueous solutions with the added catalysts were kept in the dark for some minutes to establish the adsorption equilibrium of the methyl orange for the catalyst before exposure to the simulated sunlight. After exposure to the radiation for different intervals, the UV-vis spectrophotometer (TU-1900, Beijing Purkinje General Instrument Co., Ltd.) was used to determine the solution concentration of methyl orange. The absorbance accuracy is ±0.002 Abs (0–0.5 Abs), and ±0.004 Abs (0.5–1.0 Abs).

3 Results and discussion

3.1 Structure and morphology

Fig. 1 shows the XRD patterns of prepared MoS2, BiOI and BiOI–MoS2 samples. The diffraction peaks of 14.43° (002), 33.61° (101), 39.88° (103), 53.87° (110) can be indexed to MoS2 (JCPDS card no. 01-087-2416), while 24.57° (101), 29.55° (102), 32.13° (110), 36.56° (103), 45.59° (104), 50.39° (114), 55.19° (212), 66.44° (214), 75.48° (310) diffraction peaks are belong to tetragonal phase BiOI (JCPDS card no. 00-010-0445). No peaks of other impurities are observed in the diffraction peaks of the as-prepared BiOI and MoS2, indicating that the high purity and single phase of the prepared BiOI and MoS2 products. Moreover, diffraction peaks of MoS2 can be found hardly because of its relatively low content in the prepared BiOI–MoS2 samples.

FESEM images of the MoS2, BiOI and BiOI–0.5% MoS2 samples are shown in Fig. 2.

![Fig. 1 X-ray diffraction patterns of prepared MoS2, BiOI and BiOI–MoS2 samples.](image-url)
As shown in Fig. 2(a), the synthesized MoS₂ sample structure is composed of curled and interlaced nanosheets, while BiOI and BiOI–0.5% MoS₂ samples exhibit a similar 3D flower-like hierarchical spherical structure. The flower-like structures have wide size distribution and diameters ranging from approximately 600 nm to 1.5 μm. Moreover, these microspheres are not completely isolated from each other, but often coupled together. Compare with pristine BiOI, BiOI–0.5% MoS₂ has smaller spherical size. Close examination of the morphology reveals that the hierarchical microsphere consisting of loosely stacked nanoplates with an average slide length of about 200 nm. This specific hierarchical nanostructures make the samples have an obvious high surface-to-volume ratio, which is favourable for pollutant molecules transportation and light injection.

3.2 Optical properties

The optical properties of the samples were investigated by ultraviolet-visible diffuse reflectance spectra and depicted in Fig. 3(a), and the curves of \((a\nu h)^{1/2} \text{ versus } h\) derived from the UV-visible spectra are presented in Fig. 3(b). As shown in Fig. 3(b), the loading of MoS₂ can significantly affect the band gap energy compared to pristine BiOI, and the extent of band gap energy greatly depends upon the loading level. The pristine BiOI and MoS₂ exhibit a band gap energy of 1.87 eV and 1.71 eV respectively, which is close to the values reported in other literatures. Moreover, BiOI–MoS₂ composites exhibit larger band gap energy than that of BiOI, as BiOI–MoS₂ composites exhibit a band gap energy of about 2.25 eV (BiOI–0.1% MoS₂), 2.30 eV (BiOI–0.5% MoS₂) and 2.25 eV (BiOI–1% MoS₂) respectively. Although the addition of MoS₂ in BiOI enlarged the band gap of BiOI, the absorbance of BiOI–MoS₂ samples are much stronger than that of pristine BiOI in the visible region, which allows the BiOI–MoS₂ catalysts to utilize more visible light during photocatalytic degradation and is expected to enhance the photocatalytic behavior.

3.3 Adsorption–desorption analysis

The N₂ adsorption–desorption isotherms of the pristine BiOI and BiOI–0.5% MoS₂ samples are shown in Fig. 4. Both of the isotherms exhibit a typical IV isotherm with a hysteresis loop, suggesting their mesoporous features, which is also confirmed by the corresponding pore size distribution curve (inset in Fig. 4). As shown in Table 1, the BET surface areas were calculated to be 52.87 and 48.81 m² g⁻¹ for pristine BiOI and BiOI–0.5% MoS₂ respectively. In addition, the average mesoporous diameter of BiOI–0.5% MoS₂ is larger than that of pristine BiOI. The BET surface area values did not have obvious difference, which indicates that the BET surface area has little effect on the photocatalytic performance of obtained BiOI and BiOI–0.5% MoS₂ samples.
3.4 FTIR analysis

The FTIR spectra of pure BiOI and BiOI–MoS2 hybrids are shown in Fig. 5. The peak at around 520 cm\(^{-1}\) is corresponded to the stretching vibration of the Bi–O.\(^{34}\) Compared with pure BiOI, the stretching vibration of Bi–O in BiOI–MoS2 samples shift to higher frequency region slightly, indicating that there are strong interaction between BiOI and MoS2.\(^{34,42}\) The strong interaction between BiOI and MoS2 may be beneficial to the separation of photo-induced charge carriers. In addition, the peak at around 1620 cm\(^{-1}\) is ascribed to the bending vibration absorption of free water molecules, and the broad peak at around 3420 cm\(^{-1}\) is related to the stretching vibrations of O–H,\(^{43,44}\) which could serve as anchor to the contaminant molecules.

3.5 Photocatalytic performance

The degradations of methyl orange dye by BiOI–MoS2 samples under visible light irradiation are shown in Fig. 6(a). Error bars in Fig. 6 represent SDs calculated from three parallel experiments. About 50% MO was photodegraded by pristine BiOI, and the introduction of MoS2 into BiOI can enhance the degradation efficiency. BiOI–0.5% MoS2 sample exhibits the best excellent photocatalytic activity towards MO, and the photodegradation rate could reach 95% under 90 min of visible light irradiation. Compared to other reported BiOI composites, the prepared BiOI–MoS2 composites shows higher photodegradation properties to MO as shown in Table 2.

The stability is one of the important considerations for the application of a photocatalyst. Recycling experiments on the photocatalytic degradation of methyl orange dye were carried out as shown in Fig. 6(b). The degradation rate is about 80% for the second and third cycles, while it could maintain at 60% after four successive cycles. Fig. 7 shows the microstructure of BiOI–0.5% MoS2 which had gone through four cycles photocatalysis tests. Compared with the microstructure of BiOI–0.5% MoS2 before cycles (Fig. 2(c) and (d)), there are more small particles on the surface of spherical BiOI, which indicates the disaggregation of the sponge structure of BiOI. The decrease of the photocatalytic activity may be due to the disaggregation of the sponge structure of BiOI.

Table 1 Textural features of BiOI and BiOI–0.5% MoS2 samples

<table>
<thead>
<tr>
<th>Semiconductor</th>
<th>BET surface area (m(^2) g(^{-1}))</th>
<th>Pore volume (cm(^3) g(^{-1}))</th>
<th>Average pore diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BiOI</td>
<td>52.87</td>
<td>0.23</td>
<td>13.60</td>
</tr>
<tr>
<td>BiOI–0.5% MoS2</td>
<td>48.81</td>
<td>0.24</td>
<td>16.57</td>
</tr>
</tbody>
</table>

Fig. 5 FTIR spectra of BiOI, MoS2 and BiOI–MoS2 samples.

Fig. 3 (a) UV-Vis diffused reflectance spectra of pristine MoS2, BiOI and BiOI–MoS2 samples; (b) the plots of transformed Kubelka–Munk function versus the energy of light.

Fig. 4 N\(_2\) adsorption and desorption isotherms and the corresponding pore-size distribution (inset) for the BiOI and BiOI–0.5% MoS2 samples.
Photoluminescence (PL) spectrum and photocurrent generation are effective techniques to evaluate the efficiency of charge carrier trapping, transfer and separation in semiconductor materials and surface defects of samples. Fig. 8(a) shows the room temperature PL spectra of prepared BiOI and BiOI–MoS$_2$ composites with an excitation wavelength of 325 nm. There are three intense emission peaks centered around 370 nm, 590 nm and 620 nm. The BiOI–0.5% MoS$_2$ exhibited the lowest peak intensity, while BiOI exhibited the highest peak intensity. This result implies BiOI–0.5% MoS$_2$ has the lowest rate of recombination of photogenerated charge carriers, while BiOI has the highest rate of recombination of photogenerated charge carriers.

Fig. 8(b) showed the photocurrent response of BiOI, MoS$_2$ and BiOI–0.5% MoS$_2$ with illumination of visible light. The rapid increase photocurrent response from a light-off to light-on state was mainly due to the fast separation and transfer of the photogenerated electrons on the surface of the working electrode. As shown in Fig. 8(b), the photocurrent density generated by BiOI–0.5% MoS$_2$ was much higher than that by...
BiOI, which indicate that BiOI–0.5% MoS2 has more efficiency separation rate of photogenerated carriers than BiOI. This result is consistent with the results of PL, and it could be speculated that the separation of photogenerated carriers may be one of the reasons for the highest photocatalytic performance of BiOI–0.5% MoS2 on MO degradation.

Moreover, the energy of conduction band edge ($E_{CB}$) and the energy of valence band edge ($E_{VB}$) can be calculated by using the following equations:

$$E_{CB} = -\chi + 0.5E_g$$  \hspace{1cm} (1)

and

$$E_{VB} = -\chi - 0.5E_g$$  \hspace{1cm} (2)

where, $\chi$ is the absolute electronegativity of the semiconductor, and $E_g$ is the band gap energy of the semiconductor. The absolute electronegativity of BiOI and MoS2 is 5.99 eV (ref. 8) and 5.32 eV (ref. 45) respectively. As the pristine BiOI and MoS2 exhibit a band gap energy of 1.87 eV and 1.71 eV respectively as shown in Fig. 3(b), the calculated $E_{CB}$ and $E_{VB}$ of BiOI is about $-5.05$ eV and $-6.93$ eV, while it is $-4.46$ eV and $-6.18$ eV for MoS2 respectively. Therefore, it is thermodynamically favorable for the direct electron transfer from the conduction band of MoS2 to the conduction band of BiOI, while the holes transfer from the valance band of BiOI to the valance band of MoS2 as shown in Fig. 9.

### 3.6 Photocatalytic mechanism

To survey the photocatalytic disinfection mechanism, active species trapping experiments were conducted and the results are shown in Fig. 10. Error bars in Fig. 10 represent SDs calculated from three parallel experiments. Ammonium oxalate and isopropanol were chose as $h^+$ scavengers and OH scavengers respectively. As shown in Fig. 10, comparing with the photodegradation efficiency without scavenger, the photodegradation efficiency is decreased obviously when ammonium oxalate was added into the MO solution. However, it is only a little decreased when isopropanol was added into the MO solution. This result indicates that $h^+$ was the main reactive
species in the photodegradation of MO for the prepared BiOI–
MoS2 samples under visible light irradiation.

3.7 Discussion on the effects of MoS2 on the photocatalytic activity

From Fig. 6, it is deduced that the photocatalytic activity of BiOI
increased with the loading of MoS2 on BiOI. The photocatalytic
activity of BiOI–MoS2 increases with the increase of MoS2
contents first, then it decreases when MoS2 content is over
0.5 wt%. This can be attributed to two main reasons. First, it is
thermodynamically favorable for the direct electron transfer
from the conduction band of MoS2 to the conduction band of
BiOI, while the holes transfer from the valance band of BiOI to
the valance band of MoS2 as shown in Fig. 9. Thus, the modifi-
cation of MoS2 on BiOI can accelerate the division and restrain
the recombination of photogenerated electron–hole pairs,
resulting in the improved photocatalytic activity. Second, too
much MoS2 loading on the surface of BiOI will prevent light
from reaching surface of BiOI, and thus reduce the generation
of electrons and holes. In addition, too much MoS2 loading will
also limit the efficiency of charge separation, which is
confirmed by the photoluminescence spectra of pure BiOI and
BiOI–MoS2 composites as shown in Fig. 8(a).

4 Conclusions

3D hierarchical BiOI modified by MoS2 with excellent photo-
catalytic performance in the degradation of methyl orange
under visible light irradiation were successfully fabricated
through a simple solvent thermal process. The photocatalytic
activity of BiOI–MoS2 for the degradation of methyl orange
increases with the increase of MoS2 contents first, then it
decreases when MoS2 content is over 0.5 wt%. The degradation
efficiency of methyl orange for BiOI–0.5% MoS2 is about two
times higher than that of bare BiOI nanostructures. The enhanced photocatalytic activities could be attributed to higher
separation efficiency of photogenerated charge carriers. However, radicals and holes trapping experiments showed that h+
dominate the photodegradation process of MO.

Conflicts of interest

There are no conflicts to declare.

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