**In-situ** construction of Bi$_2$S$_3$/BiOI heterojunctions with boosted photocatalytic activity

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1. **Introduction**

   Serious environmental pollution caused by the random discharge of wastewater, exhaust gas into the environment has triggered considerable attention [1–3], the deteriorated environment significantly affects the survival and development of human beings and biospheres. To achieve sustainability of human society, it is crucial to purify the environment. Up to now, massive strategies have been applied to treat contaminants and create a comfortable environment for human society [4–6]. Among the various methods, photocatalytic technology has attracted considerable interest owing to its inherent advantages, such as low power consumption, safe, easy to operation, environmentally friendly and relative high efficiency [7–9]. Tremendous studies have shown that photocatalytic technology is one of the promising strategies to destruct pollutants [10–12]. To implement high-efficiency photocatalysis, fabrication and development of highly efficient photocatalysts is the core step. Amongst the massive photocatalysts, BiOI has drawn intense attention in light of its layered structure and strong visible light response ability [13–15]. However, BiOI suffers from low photocatalytic activity owing to the low separation rate of carriers [16–18]. To meet the practical application of BiOI, it is significant to elevate the photocatalytic activity of BiOI by ameliorating the separation of carriers. Extensive approaches have been used to boost the separation of photoinduced carriers, such as doping [19], construction of defects [14,20], morphology regulation [21], and building of heterojunctions [22,23], and so on. Among all these approaches, construction of heterostructures is deemed as one of the practical methods to boost the activity of BiOI [24–26]. Construction of BiOI-based heterojunctions demands another photocatalyst that can match the band structure of BiOI, thus an interfacial electric field will be established, facilitating the separation of photoinduced carriers and boosting the activity.

   Amongst the various photocatalysts, Bi$_2$S$_3$ is an ideal candidate to couple with BiOI. Bi$_2$S$_3$ is a photocatalyst with narrow bandgap (~1.3 eV) and a layered structure [27,28], the unique features endow with Bi$_2$S$_3$ strong response to...
visible light and high photocatalytic activity. Naturally, Bi$_2$S$_3$ is widely employed to couple with other semiconductors to construct heterojunctions, largely ameliorating the photocatalytic ability of the heterostructures, for example, Bi$_2$S$_3$/BiOI [28], Bi$_2$S$_3$/SnS$_2$ [31] and so on.

Under a hydrothermal environment, Bi$_2$S$_3$/BiOI heterojunctions were prepared by a hydrothermal method using l-cysteine and KI. The results show that Bi$_2$S$_3$/BiOI heterojunctions demonstrate significantly enhanced on the 2%-Bi$_2$S$_3@1%$-GO/BiOI ternary nanocomposite. Cao et al. [33] fabricated Bi$_2$S$_3$/BiOI heterostructures through a facile and economical ion exchange method between BiOI and thioacetamide (CH$_3$CSNH$_2$), the optimal content of Bi$_2$S$_3$ is 4% with maximal photocatalytic degradation efficiency of 81.9% (5 h). Fang et al. [34] prepared BiOI/Bi$_2$S$_3$ heterojunctions by a soft chemical route using BiOI and thioacetamide. Wang et al. [35] prepared Bi$_2$S$_3$/BiOI by a facile wet chemical route between BiOI and l-cysteine, thus Bi$_2$S$_3$ exists in the composites. Fig. 1C shows the XRD results, it is obvious that Bi$_2$S$_3$/BiOI heterojunctions have peaks for Bi$_2$S$_3$ were detected, which can be attributed to Bi$_2$S$_3$. From XRD patterns of the samples, no diffraction peaks were detected, indicating high purity of the samples.

In this paper, Bi$_2$S$_3$/BiOI composites were in-situ fabricated by a hydrothermal method using l-cysteine and KI. Under a hydrothermal environment, Bi$_2$S$_3$/BiOI heterojunctions will be in-situ formed with strong interface interaction. The Bi$_2$S$_3$/BiOI heterojunctions built will be carefully studied by several methods, photocatalytic activities of the samples were evaluated by decontamination of Rhodamine B (RhB). The results show that Bi$_2$S$_3$/BiOI heterojunctions demonstrate higher activity than the reference BiOI, and the composites exhibit excellent stability. Construction of Bi$_2$S$_3$/BiOI heterojunctions using l-cysteine is a reliable strategy to boost the activity of BiOI, this method can be applied to prepare other highly efficient photocatalysts.

2. Experimental sections

Detailed information was provided in the Supporting Information.

3. Results and discussion

3.1. Characterization

The specific surface area of the samples is demonstrated in Table 1. Clearly, the specific surface area of the samples gradually increases as the loading of l-cysteine, which firmly shows that adding l-cysteine into the preparation system of BiOI dramatically affects the crystal growth of BiOI, resulting in relatively high specific surface area. Commonly, a high specific surface area is favorable for photocatalytic activity [36]. However, in light of the photocatalytic activity, specific surface area is not the leading factor that determines the photocatalytic performance in this case.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$S_{BET}$ (m$^2$/g)</th>
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<tbody>
<tr>
<td>BiOI</td>
<td>1.6</td>
</tr>
<tr>
<td>5%</td>
<td>2.6</td>
</tr>
<tr>
<td>10%</td>
<td>1.5</td>
</tr>
<tr>
<td>15%</td>
<td>2.1</td>
</tr>
<tr>
<td>20%</td>
<td>2.4</td>
</tr>
</tbody>
</table>

X-ray diffraction (XRD) information of the samples is revealed in Fig. 1. As illustrated in Fig. 1A, evidently, the 0% sample corresponds to the BiOI (PDF# 10-0445), no other peaks were detected, indicating high purity of the samples. Compared to the reference BiOI, the diffraction peaks for the (001) plane of the composites become stronger, which strongly affirms that Bi$_2$S$_3$ influences the crystal growth of BiOI. From XRD patterns of the composites, no diffraction peaks for Bi$_2$S$_3$ were detected, which can be attributed to the low content of Bi$_2$S$_3$ or high dispersion on the surface of BiOI. To confirm the existence of Bi$_2$S$_3$ in the composites, the XRD profiles of the sample prepared with high molar ratio of S/Bi (3/1) is shown in Fig. 1B, compared with the standard diffraction peaks of Bi$_2$S$_3$ (PDF 75-1306), the sample with 3/1 molar ratio of S/Bi exhibits typical diffraction peaks of Bi$_2$S$_3$, which indicates that Bi$_2$S$_3$ can be obtained by a hydrothermal method using Bi(NO$_3$)$_2$. $\nu$, the wavelength of the light, is given by the Planck’s law $\nu = \frac{h}{\lambda}$, where $h$ is Planck’s constant and $\lambda$ is the wavelength. The optical properties of the photocatalysts were studied, and the results are revealed in Fig. 3A. Clearly, the absorption edge of the photocatalyst appears to red-shift as the loading of Bi$_2$S$_3$ elevates owing to the narrow bandgap of Bi$_2$S$_3$. Enhanced light absorption capacity is conducive to photocatalytic activity. In the $\alpha$hv = A(ν–$E_g$)$^y$ formula, where
\( h, v \), and \( A \) stand for the absorption coefficient, Planck coefficient, optical frequency and constants, respectively. In the equation for indirect semiconductors, \( \eta \) is equal to 2 [37,38]. Bandgaps of all the samples can be calculated according to \( \alpha h v = A (h v - E_g)^2 \) [39], as shown in Fig. 3B, the bandgap of BiOI and the 15% sample is 1.29 and 1.38 eV, separately. The narrowed bandgap of the 15% sample is allocated to the existence of Bi\(_2\)S\(_3\) in the composites and the bandgap of Bi\(_2\)S\(_3\) is narrower than that of BiOI. Generally, a narrow bandgap is beneficial to solar light-driven photocatalytic activity.

During the photocatalytic process, so many factors can determine the photocatalytic activity, among all the factors, the separation of the photoinduced carriers performs a leading role in determining the photocatalytic activity of the photocatalyst, consequently, it is absolutely necessary to study the separation behaviors of photogenerated carriers. Surface photovoltage spectroscopy (SPS) responses of the samples induced under light irradiation are shown in Fig. 4A, it is evident that all the photocatalysts display detectable SPS from 300 to 600 nm, which can be assigned to the jump of electrons from the valence band to the conduction band, which generates the change in the surface potential barrier, displaying SPS signals. All the Bi\(_2\)S\(_3\)/BiOI composites exhibit stronger SPS signals than the reference BiOI, more importantly, the Bi\(_2\)S\(_3\)/BiOI heterojunctions possess obvious SPS response from 600 to 700 nm. Clearly, the enhanced SPS strength and range of SPS is definitely allocated to the existence of Bi\(_2\)S\(_3\) in the composites. The SPS signal intensity of the sample gradually elevates as the loading of Bi\(_2\)S\(_3\) boosts, among all the photocatalysts, the 15% photocatalyst holds the strongest SPS response. However, SPS response begins to drop as the amount of Bi\(_2\)S\(_3\) further increases. Excessive Bi\(_2\)S\(_3\) on the surface of BiOI will inhibit the light from penetrating the interface of Bi\(_2\)S\(_3\)/BiOI, holding low SPS signals. According to the measurement principle [40], a strong SPS response designates a high separation rate of photoexcited carriers. Generally, a high separation rate of photoactivated carriers is favorable for the photocatalytic activity, thereby, it is anticipated that the 15% sample will possess the highest activity. To further investigate the separation property of carriers, the photocurrent generated by the samples under simulated sunlight irradiation was measured. As revealed in Fig. 4B, photocurrent intensity of the 15% sample is higher than that of the reference BiOI, which agrees well with SPS results. Presented in Fig. 4C, in comparison with the reference BiOI, the 15% photocatalyst holds obviously smaller impedance, which implies that the 15% photocatalyst has lower migration resistance for photoinduced electrons than the reference BiOI, which is advantageous to the separation of photoexcited carriers, according well with photocatalytic activity.
3.2. Photocatalytic activity measurement

Photocatalytic performance of the photocatalysts was investigated by destruction of RhB under simulated sunlight illumination. As shown in Fig. 5A, the adsorption–desorption equilibrium of Rhodamine B over the sample can be quickly established, and Rhodamine B can be effectively destructed over the photocatalysts, the decay of RhB over the sample can be mainly allocated to photocatalysis. Amongst the samples, the 15% sample has the highest activity. The decontamination of RhB on the photocatalyst can
be described by a first-order kinetic, namely, 

$$\ln\left(\frac{C_0}{C_t}\right) = kt,$$

where $C_0$ and $C_t$ is the concentration of Rhodamine B before irradiation and the concentration of Rhodamine B at the moment after light irradiation, respectively, while $k$ is the degradation rate constant of RhB. High $k$ indicates high photocatalytic activity. As demonstrated in Fig. 5B, all the Bi$_2$S$_3$/BiOI samples display higher activity than the reference BiOI, and the 15% photocatalyst holds the highest activity, the activity of the 15% sample is 2.7 times of that of the blank BiOI. Interestingly, the trend in photocatalytic activity fits well with the results of the separation of photoinduced carriers, confirming that the separation of photoinduced carriers plays a leading role in influencing the activity of photocatalysts. However, excessive Bi$_2$S$_3$ loading on the BiOI surface interferes with photoexcitation, thus activity of the 20% catalyst is lower than that of the 15% catalyst. This result is consistent with the previous XRD, UV and SPS test results. From the above results, it is apparent that coupling
Bi$_2$S$_3$ with BiOI by a facile hydrothermal approach is a reliable strategy to boost the activity of BiOI.

As shown in Fig. 6A, the degradation efficiency of RhB on the catalyst varies at different pH, and the degradation efficiency of Rhodamine B is highest at pH = 7.0. The degradation efficiency of Rhodamine B is inhibited at both pH = 2 and pH = 12. Fig. 6B shows that the degradation efficiency is partially inhibited when the dosage of catalyst due to the scattering effect of particles. As demonstrated in Fig. 6C, the highest degradation rate is observed when the concentration of RhB is 10 mg/L, and the degradation efficiency is suppressed by gradually increasing concentration.

![Image](image1.png)

**Fig. 6.** (A) Degradation rates of catalyst at different pH conditions, (B) degradation rates of catalyst at different dye concentrations, (C) degradation rates at different catalyst dosages, and (D) effect of different catalysts on chemical oxygen demand removal (The contaminant is Rhodamine B and the light source is a xenon lamp).

![Image](image2.png)

**Fig. 7.** Cycle experiment (A) and X-ray diffraction patterns photocatalytic cycles (B) of the 15% sample.
of Rhodamine B. In Fig. 6D, after irradiation for 180 min, the chemical oxygen demand (COD) removal of Rhodamine B on the 0% and 15% catalysts is 23.2% and 56.3%, respectively, which indicates that activity of the composite catalysts is enhanced and the COD removal rate increases significantly.

Stability of the photocatalyst is an important factor which influences the practical application of photocatalyst. Cycle experiments for the 15% sample were performed. As demonstrated in Fig. 7A, after five cycles, no obvious drop-in photocatalytic activity was observed, firmly affirming the stability of the samples originated from strong interaction between Bi$_2$S$_3$ and BiOI. XRD patterns of the 15% sample before and after the photocatalytic cycle are illustrated in Fig. 7B, no new peaks appear. The results strongly support the stability of the sample, and the photocatalysts have promising applications in wastewater purification.

4. Conclusion

In this work, Bi$_2$S$_3$/BiOI heterojunctions were in-situ constructed by a facile hydrothermal method with the assistance of l-cysteine. Fabrication of Bi$_2$S$_3$/BiOI heterojunctions can be solidly proved by XRD and EDS. Integration of Bi$_2$S$_3$ with BiOI promotes the specific surface area, on the whole, widens the light response range, and boosts the separation of photoinduced carriers. All the Bi$_2$S$_3$/BiOI heterostructures show higher photocatalytic activity than BiOI, when the molar ratio of S/Bi is 15%, the sample displays the highest activity for detoxification of RhB, which is 2.7 times of that of BiOI. Moreover, the composites have excellent stability. This work offers a significant strategy to in-situ constructing heterostructures containing Bi$_2$S$_3$.

Data availability statement

The authors confirm that the data supporting the findings of this study are available within the article.

Acknowledgment

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References


Supporting information

1. Experimental sections

All the chemicals are analytical reagent and were obtained from Chengdu Kelong Chemicals Co., Ltd., (Chengdu, China). 4.1 g Bi(NO3)3·5H2O was dissolved in 40 mL glacial acetic acid, forming solution A. 1.4 g KI and desired l-cysteine were dissolved in 20 mL deionized water, obtaining solution B, the molar ratio of S/Bi is 0%, 5%, 10%, 15%, and 20%, respectively. Under intense agitation, solution B was dropped into solution A, and then the suspension system was continuously stirred for 1 h. Afterward, the suspension was transferred into a 100 mL PTFE lined autoclave and kept at 180°C for 24 h. After the autoclave cooling down to room temperature, the samples were acquired by filtering, rinsing with deionized water, and ethanol for many times. The samples were obtained by drying at 80°C overnight. The sample was fabricated with different molar ratios of S/Bi was designed as 0% (BiOI), 5%, 10%, 15%, and 20%, respectively.

Specific surface area of the sample was determined on an SSA-4200 tester. The crystal information was attained on a D2 PHASEX X-ray diffractometer (Bruker). Morphologies of the samples were observed on a VEGA3 SBU scanning electron microscopy with energy-dispersive X-ray spectroscopy. The optical properties were studied on a UH4150 UV-Vis spectrophotometer using BaSO4 as the reference. Separation behavior of the carriers was measured on a self-assembled surface photovoltage spectroscopy and a CHI660E electrochemical workstation with a 500 W xenon lamp.

Photocatalytic performance of the catalysts was evaluated by destruction of Rhodamine B (RhB) under a 500 W xenon lamp (simulated solar light). The initial mass concentration of Rhodamine B solution was 10 mg/L, the dosage of photocatalyst was 1 g/L. Before the photocatalytic reaction, the suspension system was stirred for 30 min in dark to establish adsorption–desorption equilibrium. At regular time-span, intervals, 5 mL the turbid solution was sampled, after centrifuging, the residual RhB was analyzed on a TU-1950 UV-Vis spectrophotometer. Total organic carbon (TOC) of RhB solution was tested using a Vario TOC analyzer.