

剥离蒙脱石表面原位构建 $\text{Bi}_2\text{O}_3/\text{Bi}_2\text{SiO}_5$ 异质结及其光催化活性聂 涛^{1,2}, 余 婧^{1,2}, 陈 犇^{1,2}, 汪 锐^{1,2}, 贺贝贝^{1,2}, 金 俊^{1,2}, 王欢文^{1,2}, 公衍生^{1,2}

(1. 中国地质大学(武汉)纳米矿物材料及应用教育部工程研究中心, 武汉 430074;

2. 中国地质大学(武汉)材料与化学学院, 武汉 430074)

摘 要: 采用一步法, 在剥离蒙脱石表面原位构建了 $\text{Bi}_2\text{O}_3/\text{Bi}_2\text{SiO}_5$ 异质结, 系统研究了其物相结构、微观形貌和光学特征。制备过程中, 剥离蒙脱石除作为 $\text{Bi}_2\text{O}_3/\text{Bi}_2\text{SiO}_5$ 异质结生长的骨架, 还可以作为硅源得到 Bi_2SiO_5 。结果表明: 与纯 $\alpha\text{-Bi}_2\text{O}_3$ 相比, 在模拟太阳光的照射下, $\text{Bi}_2\text{O}_3/\text{Bi}_2\text{SiO}_5$ 异质结表现出对罗丹明 B 有优良降解性能, 这主要是由于 Bi_2O_3 与 Bi_2SiO_5 之间形成的 p-n 结以及高的比表面积所引起的。此外, 还提出了光催化反应机理。本工作提供了一种构建低成本污染物降解催化剂的新方法, 拓展了蒙脱石的新应用。

关键词: 剥离蒙脱石; 异质结; 原位合成; 染料污染物降解

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In-situ Construction and Photocatalytic Activity of $\text{Bi}_2\text{O}_3/\text{Bi}_2\text{SiO}_5$ Heterojunction on Exfoliated Montmorillonite

NIE Tao^{1,2}, YU Jing^{1,2}, CHEN Ben^{1,2}, WANG Rui^{1,2}, HE Beibei^{1,2}, JIN Jun^{1,2}, WANG Huanwen^{1,2}, GONG Yansheng^{1,2}

(1. Engineering Research Center of Nano-Geomaterials of Ministry of Education, China University of Geosciences, Wuhan 430074, China; 2. Faculty of Materials Science and Chemistry, China University of Geosciences, Wuhan 430074, China)

Abstract: $\text{Bi}_2\text{O}_3/\text{Bi}_2\text{SiO}_5$ heterojunction was *in-situ* constructed on exfoliated montmorillonite via an one-pot method. The crystal structure, morphology, and optical features for the as-synthesized $\text{Bi}_2\text{O}_3/\text{Bi}_2\text{SiO}_5$ heterojunction were characterized. In the preparation process, the exfoliated montmorillonite acts as Si source and framework for the *in-situ* formation of $\text{Bi}_2\text{O}_3/\text{Bi}_2\text{SiO}_5$ p-n heterogeneous junction on montmorillonite interlayer. As a result, $\text{Bi}_2\text{O}_3/\text{Bi}_2\text{SiO}_5$ photocatalyst exhibits a superior photocatalytic performance rather than bare $\alpha\text{-Bi}_2\text{O}_3$ for the degradation of Rhodamine B (RhB) via the simulated solar light irradiation due to the synergetic effects of large specific surface areas and p-n junction between Bi_2SiO_5 and Bi_2O_3 . Moreover, a possible photocatalytic mechanism for the as-prepared photocatalysts was proposed. This work provides a new insight into synthesizing the cost-efficient photocatalyst with montmorillonite for the contaminant degradation.

Keywords: exfoliated montmorillonite; heterojunctions; *in-situ* synthesis; dye pollutant degradation

1 Introduction

The existing environmental pollution originating from dye contaminants becomes a dramatic problem to the eco-environment and human beings^[1-3]. Some efforts have been devoted to eliminate or minimize the environmental pollution^[4-6]. Among the reported methods, the semiconductor photocatalytic technology

is an economical and friendly strategy for the environmental remediation, which has attracted considerable attentions^[7-9]. More importantly, a photocatalyst with cost-effective and efficient activity is a core of semiconductor-based photocatalysis.

As a phase of Aurivillius family with the layered structure, Bi_2SiO_5 is extensively investigated due to its nontoxicity, chemical stability and excellent photocatalytic

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第一作者: 聂 涛(1994—), 男, 硕士研究生。

通信作者: 公衍生(1977—), 男, 博士, 副教授。

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First author: NIE Tao (1994—), male, Master candidate.

E-mail: 919387344@qq.com

Correspondent author: GONG Yansheng (1977—), male, Ph.D., Associate Professor.

E-mail: gongysh@cug.edu.cn

behaviors^[10–11]. However, pristine Bi₂SiO₅ can only absorb the ultraviolet light because of its broad band gap (~3.5 eV)^[12–13]. Therefore, it is essential to expand the photo-absorption range of Bi₂SiO₅-based photocatalysts to further harvest the solar energy. In recent years, various effective strategies have been proposed to enhance the visible-light absorption of Bi₂SiO₅^[14–16]. Among them, a constructed heterojunction photocatalyst is proved to be a reliable approach, having an improved photocatalytic property^[17–18]. Bismuth-based oxide photocatalysts are considered as an effective candidate for the visible light driven photocatalysis due to their excellent optical response in a wide spectral range^[19–22]. Compared with other Bi-based photocatalysts, bismuth oxide (Bi₂O₃) is proved as an ideal photocatalyst with a narrow band gap and matching band potentials to form the heterojunction with Bi₂SiO₅^[23–24]. Bi₂O₃ has four kinds of crystal forms including monoclinic α , tetragonal β , body-centered cubic γ and face-centered cubic δ ^[25]. Thereinto, α -Bi₂O₃ is n-type semiconductor photocatalyst with a bandgap of 2.8 eV, while β -Bi₂O₃ is p-type semiconductor photocatalyst with a bandgap of 2.4 eV, which can act as an effective candidate for the visible light induced photocatalysis^[26–28]. Therefore, it could be anticipated that the photocatalytic performance of Bi₂SiO₅ can be notably enhanced by the construction of Bi₂O₃/Bi₂SiO₅ heterojunctions. Especially, the p-n heterojunction formed among p-type β -Bi₂O₃ and n-type Bi₂SiO₅ can facilitate the separation of photo-induced carriers in the complex photocatalyst due to its inner electric field.

At present, Bi₂O₃/Bi₂SiO₅ heterojunctions can be prepared by different efficient strategies. For instance, Lu *et al*^[29] exhibited a one-step calcination method for the fabrication of Bi₂O₃/Bi₂SiO₅ p-n heterojunction employing Bi(NO)₃ and nano-SiO₂ as precursors. Zhang *et al*^[30] constructed Bi₂O₃/Bi₂SiO₅ nanoheterostructure by mesoporous SiO₂ microspheres. Cheng *et al*^[31] investigated the photocatalytic performance of Bi₂SiO₅-Bi₂O₃ hybrid loaded sepiolite photocatalysts prepared by a chemical precipitation method. Dou *et al*^[32] obtained 3D microsphere-like Bi₂O₃/Bi₂SiO₅ microsphere heterojunctions with rich oxygen vacancies by a facile one-pot solvothermal approach. The results above indicate the superiority of heterojunctions in the photoactivity improvement of Bi₂O₃/Bi₂SiO₅. However, Bi₂O₃ particles are easy to be agglomerated, which leads to the large size of Bi₂O₃ agglomerates for the interfacial reaction, thus greatly restricting the photo-deduced carrier separation efficiency of Bi₂O₃. Moreover, the above-mentioned preparation methods are tedious using costly raw materials. Therefore, it is necessary to develop a facile and cost-effective approach to construct Bi₂O₃/Bi₂SiO₅ heterojunctions.

Montmorillonite is a hydrophilic natural mineral and often applied as a substrate to deposit the photocatalysts due to its abundant, cheap, non-toxic and environmentally friendly features^[33–35]. Montmorillonite

consists of 2:1 piled layer of two silicon oxide tetrahedrons with a sandwiched alumina octahedron^[36]. The isomorphous substitution of Al³⁺ by Si⁴⁺ in the tetrahedral layer and Mg²⁺ or Zn²⁺ by Al³⁺ inside the octahedral layer causes in the negative charge on montmorillonite surface^[37]. Compared with other clay minerals, montmorillonite has an effective adsorption performance and sufficient adsorption/exchange sites between the layers on the outer surface and edges^[38], which is widely used in wastewater treatment or purification. In addition, some previous studies showed that montmorillonite can be served as an effective substrate for the synthesis of high-performance photocatalysts, for instance, ZnO/bentonite^[39], BiFeO₃-Bi₂Fe₄O₉/bentonite^[40], MoS₂/bentonite^[41], TiO₂/montmorillonite^[42], *etc.*. These studies indicate that the photocatalysts can be uniformly dispersed in the solution after being combined with montmorillonite to produce distinct reaction sites. However, photocatalyst embedded into the interlayer of montmorillonite is not favorable for the photon's absorption, thereby affecting the improvement of its photocatalytic activity. Ma *et al*^[37] used NaF to exfoliate the bentonite, exposing the interlayer of bentonite to the outside, thereby improving the photocatalytic activity. However, all the aforementioned studies only used montmorillonite as a substrate without actually utilizing the elements inside the montmorillonite^[42–43]. Although some researchers extracted SiO₂ from montmorillonite by strong acid and high-temperature treatment as a catalytic material, the strong acid use and high-temperature treatment could consume energy and pollute the environment^[44].

In this work, Bi₂O₃/Bi₂SiO₅ heterojunctions were synthesized *via* one-step calcination with exfoliated montmorillonite (EB) and Bi(NO₃)₃ as precursors for the photocatalytic degradation. Montmorillonite was served as a substrate, and used its internal Si elements to assist the *in-situ* formation of Bi₂O₃/Bi₂SiO₅ p-n heterojunction in montmorillonite interlayer by adjusting the reaction conditions.

2 Experimental

2.1 Raw materials

All the chemical reagents used were of analytical grade and used without any further purification. Montmorillonite as a clay mineral, Bi(NO₃)₃·5H₂O and NaF were purchased from Aladdin Co., China

2.2 Preparation of Bi₂SiO₅-Bi₂O₃-exfoliated montmorillonite (Bi₂SiO₅/Bi₂O₃/EB) photocatalysts

Montmorillonite was exfoliated by a liquid phase exfoliation approach. In the process, 20 g montmorillonite was dispersed into 0.2 L purified water with 1g NaF, and treated by ultrasound for 7 d. Afterwards, the blended solution was treated *via* centrifugation at 9 000 r/min for 5 min and rinsed with deionized water for several times. The gray solids obtained after centrifugation were named as exfoliated

montmorillonite (EB).

$\text{Bi}(\text{NO}_3)_3$ powder was obtained by treating $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ in a vacuum drying cabinet at 70°C for 12 h. Afterwards, $\text{Bi}(\text{NO}_3)_3$ powder with different weights (*i.e.*, 1, 3, 5 g and 7 g) and 0.5 g EB were mixed into a quartz agate mortar for 20 min, respectively. The mixture was transferred into a crucible in air atmosphere and heated in a muffle furnace at 600°C for 3 h with a ramp of $2^\circ\text{C}/\text{min}$. The obtained lemon products were $\text{Bi}_2\text{SiO}_5/\text{Bi}_2\text{O}_3/\text{EB}$ after cooling down to room temperature. The products with different mass of $\text{Bi}(\text{NO}_3)_3$ (*i.e.*, 1, 3, 5 g and 7 g) were named as BiSiB-1, BiSiB-3, BiSiB-5 and BiSiB-7, respectively. The BiSiB-3 samples were calcined at different temperatures (*i.e.*, 500°C , 600°C and 700°C), which were marked as BiSiB- 500°C , BiSiB- 600°C and BiSiB- 700°C , respectively. Fig. 1 shows the schematic illustration for the preparation process. Pure $\alpha\text{-Bi}_2\text{O}_3$ was obtained by the same method without any EB.

2.3 Characterizations

The crystal structure was determined by a model D8-FOCUS X-ray diffractometer (XRD, BrukerAXS, Panalytical, USA) using Cu K_α radiation. The XPS spectra and chemical status were measured by a model VG Scientific ESCALAB Mark II spectrometer (ESCALAB 250XI, Thermo Scientific, America). The morphology and composition of the as-synthesized samples were analyzed by a model SU8010 scanning electronic microscope (SEM, Hitachi, Japan) and a model TF20 transmission electron microscope (TEM, JEOL Co., Japan). N_2 adsorption/desorption of the as-prepared samples was characterized a model ASAP2460 surface area analyzer (Micromeritics Ltd., Co., USA). The optical absorbance spectra was conducted by a model Lambda35 UV-Vis diffuse reflectance spectrometer (Perkinelmer, America). The electrochemical impedance spectra (EIS) and photocurrent experiments were detected by a model CHI 660E electrochemical

workstation (Chenhua Co., China), using Na_2SO_4 as an electrolyte. Ag/AgCl electrode was employed as a reference electrode, Pt wire was used as a counter electrode, and the as-prepared catalyst loaded on FTO was used as a working electrode. The working electrode was prepared according to the following procedure: 5 mg catalyst was placed into a blended solution of $10\ \mu\text{L}$ Nafion solution (5%, mass fraction) and 0.3 mL anhydrous alcohol to form a uniform slurry under ultrasonic treatment. Afterwards, the $30\ \mu\text{L}$ slurry was uniformly coated onto FTO glass with an area of approximately $1\ \text{cm}^2$ and then dried. The EIS Nyquist plots tests were conducted in a frequency range from 0.01 to 100 000 Hz under open circuit potential conditions.

2.4 Photocatalytic activity test

The photodegradation of organic pollutant (RhB) under simulated solar light irradiation was carried out to evaluate the performance of photocatalysts. The light was provided by a 300-W Xeon-lamp. In all the tests, the photocatalyst sample (0.2 g) was dispersed into 100 mL RhB aqueous solution (20 mg/L) for the photocatalytic activity tests. Before the lighting irradiation, the solution was stirred under dark condition for 60 min to reach an adsorption/desorption equilibrium. Afterwards, 3 mL aliquot was taken out and filtered at a regular interval. To determine the corresponding RhB concentration, the maximum absorption wavelength (554 nm) was determined *via* the optical characteristic absorption (Ocean Optics, America).

2.5 Active species trapping experiments

Disodium ethylenediaminetetraacetate (EDTA), tertiary butyl alcohol, and ascorbic acid were added into the RhB solution to investigate the main active species, such as removal holes (h^+), hydroxyl radical ($\cdot\text{OH}$), and superoxide radical ($\cdot\text{O}_2^-$), respectively^[45–46]. The amount of these capture agents was 1 mmol, and the other experimental conditions were consistent with the photocatalytic activity tests.

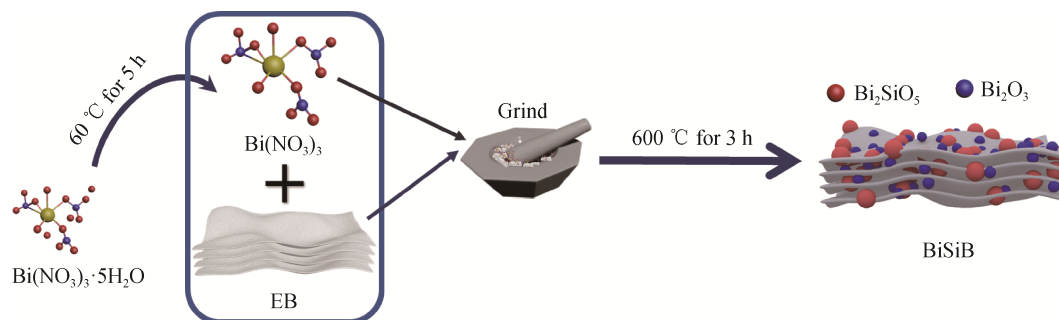


Fig. 1 Schematic illustration of the synthetic for $\text{Bi}_2\text{SiO}_5/\text{Bi}_2\text{O}_3/\text{EB}$ samples

3 Results and discussion

3.1 $\text{Bi}_2\text{SiO}_5/\text{Bi}_2\text{O}_3/\text{EB}$ photocatalysts

Fig. 2 shows the X-ray diffraction patterns of $\alpha\text{-Bi}_2\text{O}_3$, exfoliated montmorillonite and $\text{Bi}_2\text{SiO}_5/\text{Bi}_2\text{O}_3/\text{EB}$ photocatalysts, respectively. In Fig. 2(a), the

characteristic diffraction peak for EB sample as $2\theta = 8.20^\circ$ corresponds to the (001) crystal plane^[38]. For $\alpha\text{-Bi}_2\text{O}_3$, three distinct peaks with 2θ of 27.37° , 33.31° and 46.42° are referred to the ($\bar{1}21$), ($\bar{2}02$) and (041) planes of $\alpha\text{-Bi}_2\text{O}_3$ (JCPDS 71–0465), respectively. For BiSi-3, two diffraction peaks as $2\theta = 27.98^\circ$ and 32.81° are correlated to the (201) and (220) planes of $\beta\text{-Bi}_2\text{O}_3$

(JCPDS 77-5341), indicating the existence of $\beta\text{-Bi}_2\text{O}_3$ phase^[29]. Meanwhile, other three intense diffraction peaks with 2θ of 11.26° , 23.92° and 29.31° are corresponded to the (200), (310) and (311) planes of Bi_2SiO_5 (JCPDS 36-0287), respectively. In Fig. 2(d), the diffraction peaks of $\alpha\text{-Bi}_2\text{O}_3$ and $\beta\text{-Bi}_2\text{O}_3$ appear

when the calcination temperature is 500°C , while the diffraction peak of $\alpha\text{-Bi}_2\text{O}_3$ disappears, but $\beta\text{-Bi}_2\text{O}_3$ diffraction peak still exists when the temperature increases to 600°C and 700°C , indicating that Bi_2O_3 mainly exists in the crystal form of $\beta\text{-Bi}_2\text{O}_3$ phase at 600°C and 700°C .

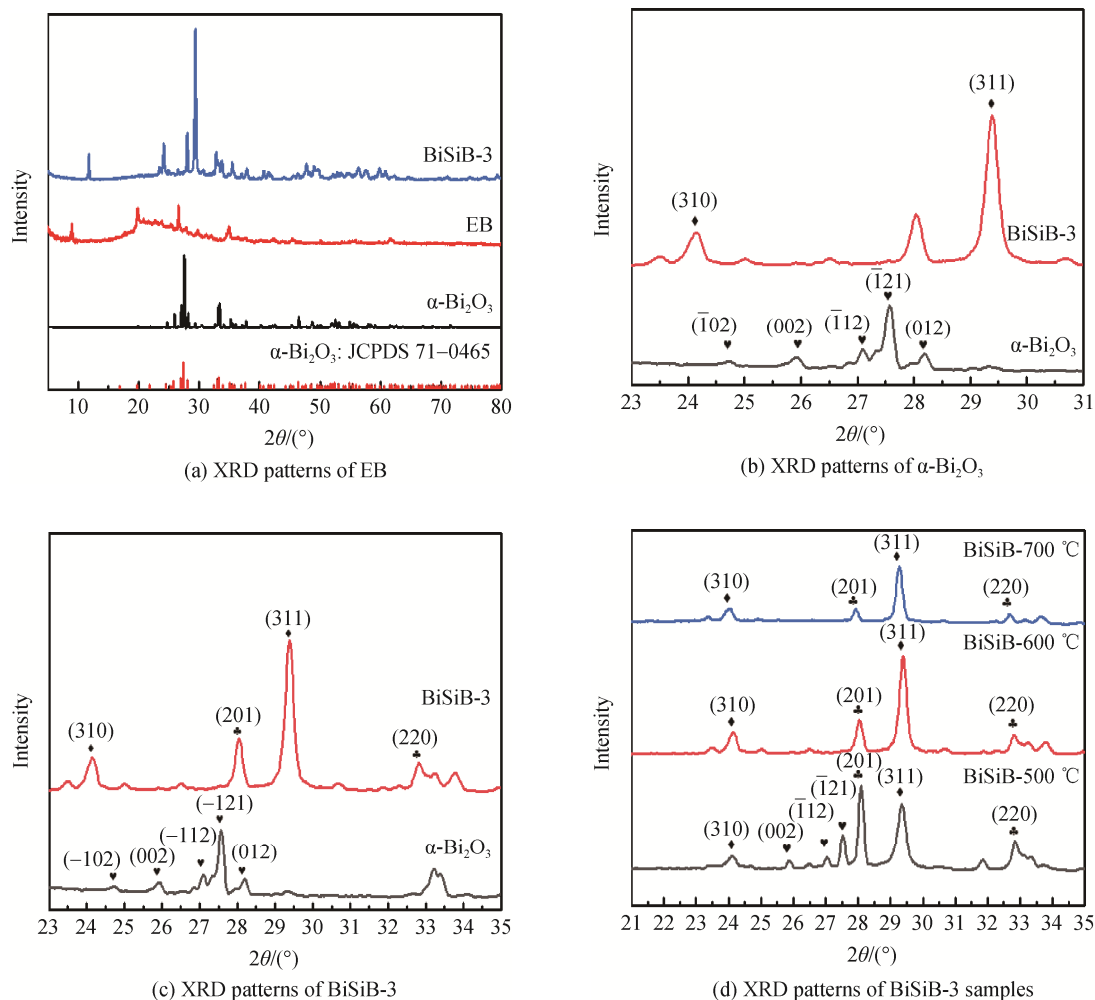


Fig. 2 XRD patterns of EB, $\alpha\text{-Bi}_2\text{O}_3$, BiSiB-3 and BiSiB-3 at different calcination temperatures

Fig. 3 shows the SEM images for EB, $\alpha\text{-Bi}_2\text{O}_3$, BiSiB-3 and BiSiB-7. In Fig. 3(a), the EB has a sheet structure with a thickness of approximately $1\ \mu\text{m}$. In Fig. 3(b), pure $\alpha\text{-Bi}_2\text{O}_3$ shows an agglomerated bulk morphology. However, after the formation of heterojunction, BiSiB-3 and BiSiB-7 samples exhibit a fluffier scattered morphology compared with pure $\alpha\text{-Bi}_2\text{O}_3$, which is beneficial for the photocatalytic activity (see Fig. 3(c) and Fig. 3(d)). Since $\text{Bi}_2\text{O}_3/\text{Bi}_2\text{SiO}_5$ heterojunction is in-situ generated on EB, the sheet morphology appears (see Fig. 3(c)). Fig. 4 shows the TEM and HRTEM images of $\text{Bi}_2\text{O}_3/\text{Bi}_2\text{SiO}_5$ heterojunction. Clearly, the fluffy scattered structure of $\text{Bi}_2\text{O}_3/\text{Bi}_2\text{SiO}_5$ heterojunction is formed. In Fig. 4(d), a distinct lattice fringes of $0.227\ \text{nm}$ corresponds to the (202) plane of Bi_2O_3 , and the interplanar spacing of $0.381\ \text{nm}$ can be indexed to the (400) plane

of Bi_2SiO_5 . Fig. 4(f) – Fig. 4(i) show the element distributions of BiSiB-3 sample. The results indicate that O, Si and Bi elements in the samples are evenly distributed, which further expounds the as-prepared sample is homogeneous.

Fig. 5(a) shows the survey X-ray photoelectron spectra of EB, $\alpha\text{-Bi}_2\text{O}_3$ and BiSiB-3, respectively. Clearly, the peaks of O, Al, and Si in EB, as well as the peak of Bi and O in $\alpha\text{-Bi}_2\text{O}_3$ appear. The peaks of O, Al, Si and Bi occur on the surface of BiSiB-3, while the element of Si does not appear in $\alpha\text{-Bi}_2\text{O}_3$. In Fig. 5(b), two intensive peaks of $159.1\ \text{eV}$ and $164.4\ \text{eV}$ are correlated to the orbitals $4f_{7/2}$ and $4f_{5/2}$ of Bi^{3+} in $\alpha\text{-Bi}_2\text{O}_3$ ^[47]. In addition, compared with $\alpha\text{-Bi}_2\text{O}_3$, the binding energy of these two peaks in BiSiB-3 is decreased by $0.2\ \text{eV}$ possibly due to the tight binding between Bi_2SiO_5 and $\beta\text{-Bi}_2\text{O}_3$, resulting in the change of

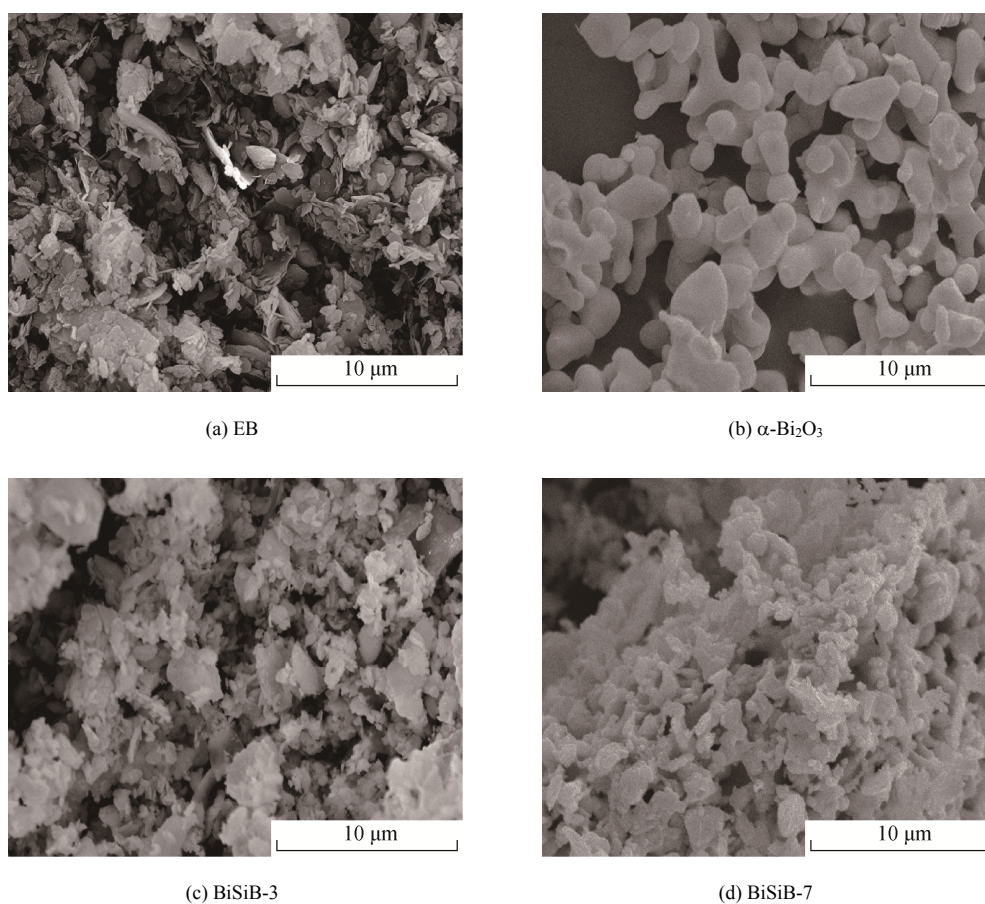
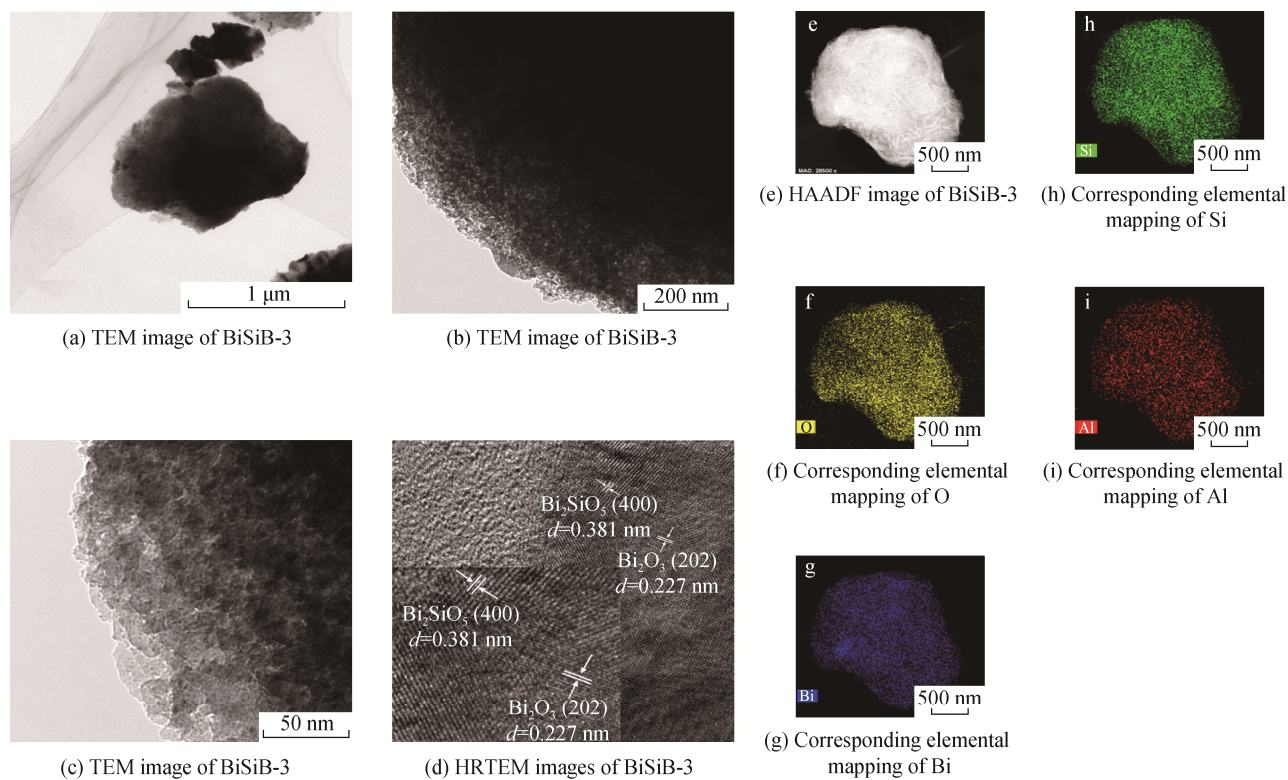
Fig. 3 SEM images of EB, α - Bi_2O_3 , BiSiB-3 and BiSiB-7 samples

Fig. 4 TEM and HRTEM images of BiSiB-3 (a, b, c, d); HAADF image of BiSiB-3 (e) and corresponding elemental mapping of O (f), Bi (g), Si (h), Al (i)

chemical state around Bi^[48]. In Fig. 5(c), the binding energy of Si 2*p* is 102.7 eV, indicating that the valence state of Si in the sample is +4. Two distinct peaks of O 1*s* in $\alpha\text{-Bi}_2\text{O}_3$ are located at 528.8 eV and 530.9 eV, which correspond to O^{2-} in $\alpha\text{-Bi}_2\text{O}_3$ (see Fig. 5(d))^[49].

For BiSiB-3, a peak at 530.1 eV in the O 1*s* energy spectrum is corresponded to Bi—O in Bi_2SiO_5 and Bi_2O_3 ^[27, 50]. Another intense peak at 532.2 eV is attributed to the adsorbed surface oxygen, which is increased by 1.3 eV, compared with $\alpha\text{-Bi}_2\text{O}_3$ ^[51–52].

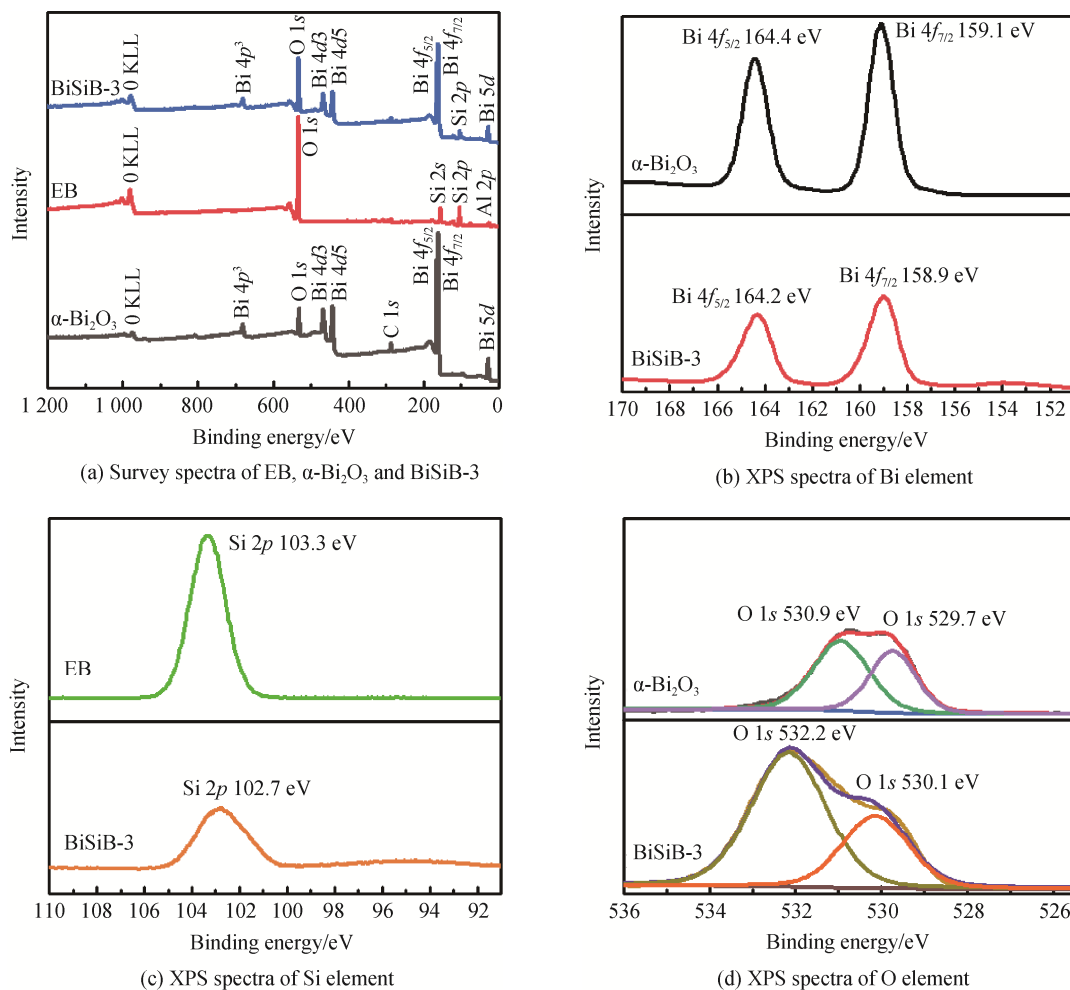


Fig. 5 XPS spectra of EB, $\alpha\text{-Bi}_2\text{O}_3$ and BiSiB-3 samples and XPS spectra of various elements

Fig. 6 shows the results of N_2 adsorption-desorption analysis of $\alpha\text{-Bi}_2\text{O}_3$ and BiSiB-3 for the determination of

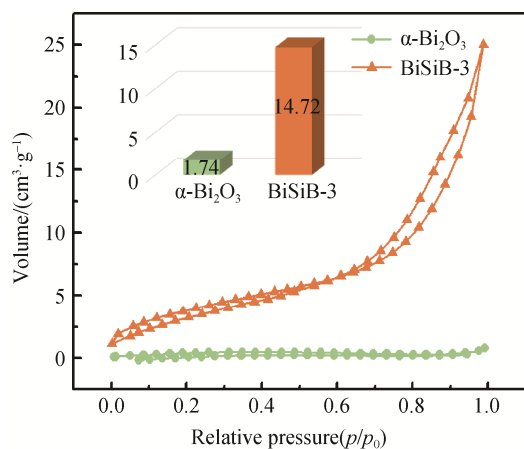


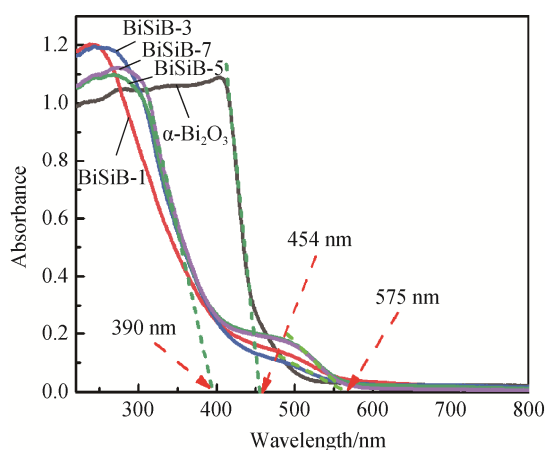
Fig. 6 N_2 sorption profiles of $\alpha\text{-Bi}_2\text{O}_3$ and BiSiB-3 for the determination of their specific surface areas (see the inserted figure)

their specific surface areas. In Fig. 6, the specific surface area of $\alpha\text{-Bi}_2\text{O}_3$ and BiSiB-3 is 1.74 m^2/g and 14.72 m^2/g , respectively. Clearly, the specific surface area of BiSiB-3 is larger than that of $\alpha\text{-Bi}_2\text{O}_3$, which is 8.5 times greater than that of $\alpha\text{-Bi}_2\text{O}_3$. The increasing specific area can improve the adsorption capacity of the catalyst for pollutants and allow more O_2 to be adsorbed on the surface, producing more O^{2-} with intense oxidizing properties under light irradiation, and thus improving the photocatalytic degradation reaction.

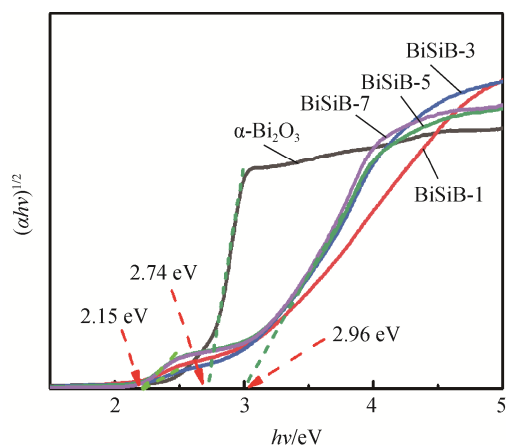
3.2 Optical and photoelectrical performance

Fig. 7 shows the UV-Vis diffuse reflectance spectra and estimated band energy spectra of $\alpha\text{-Bi}_2\text{O}_3$, BiSiB-1, BiSiB-3, BiSiB-5 and BiSiB-7. In Fig. 7, the absorption edge of $\alpha\text{-Bi}_2\text{O}_3$ is at a wavelength of 454 nm, and its corresponding bandgap is 2.74 eV. Other samples with EB exhibit two absorption edges at wavelengths of 390 nm and 575 nm, respectively, where the absorption edge at a wavelength of 575 nm is corresponded to the

bandgap of 2.15 eV for β - Bi_2O_3 , and the absorption edge at a wavelength of 390 nm is assigned to the bandgap of 2.96 eV for β - $\text{Bi}_2\text{O}_3/\text{Bi}_2\text{SiO}_5$ heterojunction. The absorption edge of bare Bi_2SiO_5 is at a wavelength of 360 nm and the associated bandgap is 3.58 eV. The absorption band edges of β - $\text{Bi}_2\text{O}_3/\text{Bi}_2\text{SiO}_5$ heterojunction are all situated between Bi_2SiO_5 and β - Bi_2O_3 , indicating that β - $\text{Bi}_2\text{O}_3/\text{Bi}_2\text{SiO}_5$ heterojunction can broaden the spectral responsive range, compared to bare Bi_2SiO_5 .



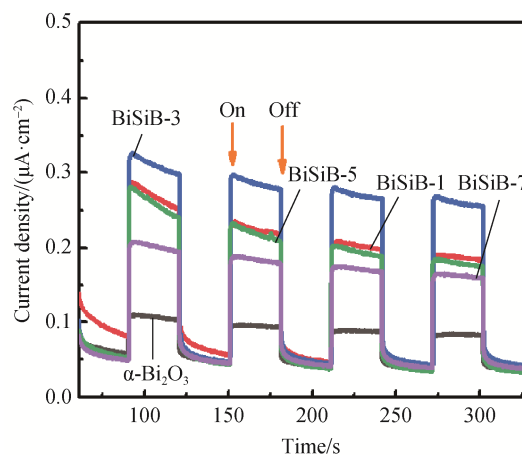
(a) UV-Vis diffuse reflectance spectra



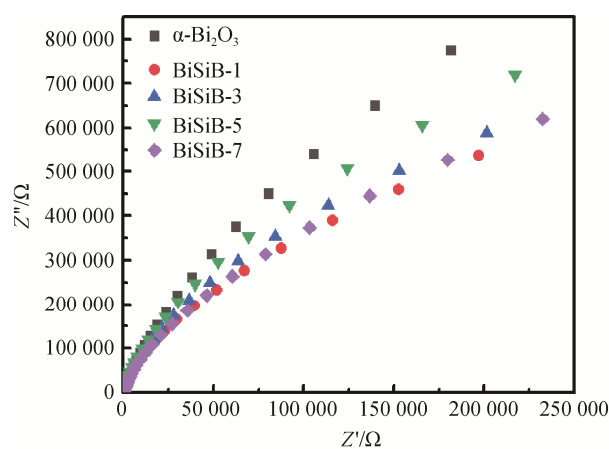
(b) Estimated band energy spectra

Fig. 7 UV-Vis diffuse reflectance spectra and estimated band energy spectra

Fig. 8 shows the photocurrent responses and EIS Nyquist plots for the as-prepared samples. In Fig. 8(a), $\text{Bi}_2\text{SiO}_5/\text{Bi}_2\text{O}_3/\text{EB}$ sample exhibits a higher photocurrent than bare α - Bi_2O_3 , indicating that $\text{Bi}_2\text{SiO}_5/\text{Bi}_2\text{O}_3/\text{EB}$ has a better photocarrier separation efficiency. In Fig. 8(b), the arc of $\text{Bi}_2\text{SiO}_5/\text{Bi}_2\text{O}_3/\text{EB}$ is smaller than that of α - Bi_2O_3 , indicating that $\text{Bi}_2\text{SiO}_5/\text{Bi}_2\text{O}_3/\text{EB}$ has a smaller resistance than α - Bi_2O_3 . These results show that β - $\text{Bi}_2\text{O}_3/\text{Bi}_2\text{SiO}_5$ heterojunction formed by the combination of Bi_2O_3 and EB can increase the photocarrier transfer and separation speed, reduce the resistance, and thus enhance its photocatalytic performance.



(a) Photocurrent responses



(b) EIS Nyquist plots for the as-prepared samples

Fig. 8 Photocurrent responses and EIS Nyquist plots for the as-prepared samples

3.3 Photocatalytic performance of $\text{Bi}_2\text{SiO}_5/\text{Bi}_2\text{O}_3/\text{EB}$ composites

The photocatalytic activities of exfoliated montmorillonite, α - Bi_2O_3 and $\text{Bi}_2\text{SiO}_5/\text{Bi}_2\text{O}_3/\text{EB}$ were investigated by degrading RhB (20 mg/L) under simulated solar light irradiation. Fig. 9(a) shows the RhB degradation dynamic curves over different photocatalysts. Pure α - Bi_2O_3 has a poor adsorption performance, but $\text{Bi}_2\text{SiO}_5/\text{Bi}_2\text{O}_3/\text{EB}$ composites exhibit a better adsorption performance after being compounded with exfoliated montmorillonite. After stirring for 60 min in dark, the adsorption rate of SiBiB-1 and SiBiB-3 reaches 78.94% and 17.61%, respectively. Under simulated solar light irradiation, pure α - Bi_2O_3 exhibits almost no photocatalytic activity over RhB. However, $\text{Bi}_2\text{O}_3/\text{Bi}_2\text{SiO}_5$ heterojunction formed with exfoliated montmorillonite has an intense degradation performance for RhB.

Among the as-prepared photocatalysts, BiSiB-3 sample shows the optimum photocatalytic activity with a removal efficiency of 96.89%. And the decomposition efficiency for the RhB is 0.0148 min^{-1} , which is 49 folds

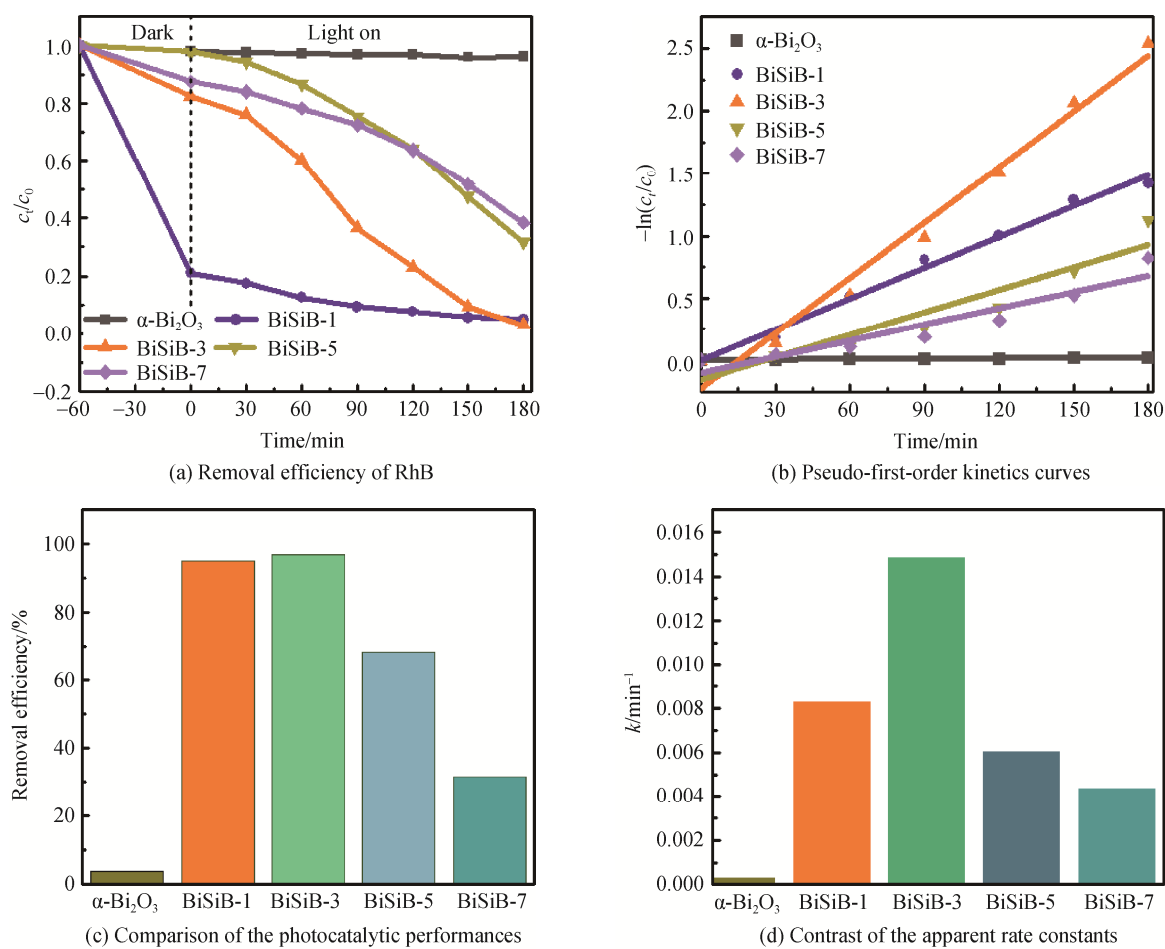


Fig. 9 Removal efficiency of RhB, pseudo-first-order kinetics curves over different samples, comparison of the photocatalytic performances toward degrading RhB solution, contrast of the apparent rate constants of $\alpha\text{-Bi}_2\text{O}_3$ and $\text{Bi}_2\text{SiO}_5/\text{Bi}_2\text{O}_3/\text{EB}$ for the degradation of RhB

than that of $\alpha\text{-Bi}_2\text{O}_3$ (see Fig. 9(d)). Furthermore, in Fig. 9(c), the decolorization proportion is 94.92%, 68.35% and 61.61% for the BiSiB-1, BiSiB-5 and BiSiB-7 samples after the irradiation of 180 min, respectively. The results indicate that $\text{Bi}_2\text{O}_3/\text{Bi}_2\text{SiO}_5$ heterojunction increases the specific surface area to enhance the adsorption capacity, and improves the separation efficiency of the photogenerated carriers, thereby enhancing the photocatalytic property.

To further investigate the photocatalytic performance, the reaction kinetics of RhB removal were analyzed. The kinetic rate constant value was calculated by the pseudo-first-order model $(-\ln(c_t/c_0) = kt)$,^[54] where c_0 and c_t are the original and instantaneous concentrations of RhB, respectively, and k is a kinetic constant. In Fig. 9(b) and 9(d), the kinetic constants of BiSiB-1 (*i.e.*, $k = 0.0083 \text{ min}^{-1}$), BiSiB-3 (*i.e.*, $k = 0.0148 \text{ min}^{-1}$), BiSiB-5 (*i.e.*, $k = 0.006 \text{ min}^{-1}$) and BiSiB-7 (*i.e.*, $k = 0.0043 \text{ min}^{-1}$) for RhB are 27.6 times, 49.3 times, 20 times and 14.3 times greater than that of bare $\alpha\text{-Bi}_2\text{O}_3$ (*i.e.*, $k = 0.0003 \text{ min}^{-1}$), respectively. It is indicated that $\text{Bi}_2\text{O}_3/\text{Bi}_2\text{SiO}_5$ heterojunction can improve the photocatalytic property, compared with $\alpha\text{-Bi}_2\text{O}_3$. Moreover, the decomposition kinetic constant of BiSiB-3 to RhB is 1.8,

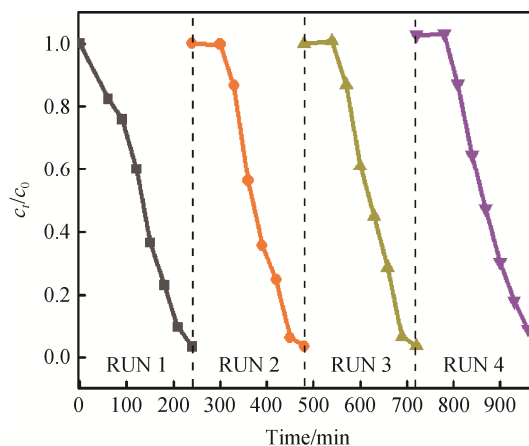
2.5 and 3.4 times greater than that of BiSiB-1, BiSiB-5 and BiSiB-7 samples, indicating that BiSiB-3 has the maximum photocatalytic performance toward the RhB degradation.

To investigate the stability and reusability of $\text{Bi}_2\text{SiO}_5/\text{Bi}_2\text{O}_3/\text{EB}$ sample, the recycling experiments were performed. In this procedure, all the parameters remain the same. In Fig. 10(a), the photocatalytic efficiency of BiSiB-3 still achieves 91.0% after four cycles. Moreover, the morphology and the sample size do not change obviously. In addition, after the photocatalytic tests for four times, the XRD patterns of BiSiB-3 (see Fig. 10(b)) also have no change. The above-mentioned results indicate that the as-prepared sample has a good stability.

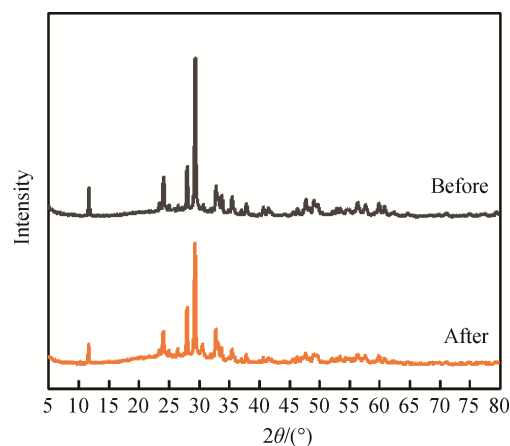
The capture experiments of the active species were used to prove the photocatalytic degradation of the main active species in RhB. Tert-butanol, ascorbic acid and disodium ethylenediaminetetraacetate (EDTA-2Na) were used as sacrificial agents of hydroxyl radical ($\cdot\text{OH}$), superoxide radical ($\cdot\text{O}_2^-$) and hole (h^+) in the photodegradation process of RhB, respectively. In Fig. 10(c) and Fig. 10(d), the RhB degradation rate decreases from 79.29% to 73.30%, 37.25% and 5.05%,

when tert-butanol, ascorbic acid and EDTA-2Na are added to the photocatalytic degradation system, respectively. The

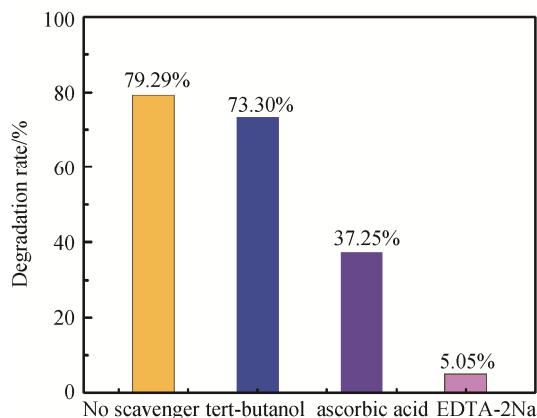
results demonstrate that h^+ and $\cdot O_2^-$ are the principal active species for the photocatalytic degradation of RhB system.



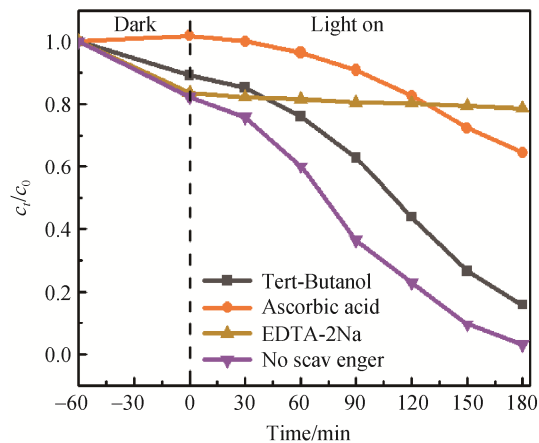
(a) Reusability experiments of BiSiB-3 sample



(b) XRD of BiSiB-3 after four photocatalytic cycles



(c) Trapping experiments of BiSiB-3 sample



(d) Effect of scavenger on the degradation of RhB

Fig. 10 Reusability experiments toward the degradation of RhB solution over BiSiB-3 (a), XRD of BiSiB-3 after four photocatalytic cycles (b), trapping experiments of photocatalytic reactions of RhB on BiSiB-3 (c), (d)

The improvement of photocatalytic performance is primarily due to the following four aspects. First, Bi_2SiO_5 is a canonical n-type semiconductor and $\beta-Bi_2O_3$ is a p-type semiconductor. Therefore, Bi_2SiO_5 and $\beta-Bi_2O_3$ can construct a p-n heterogeneous junction, which can effectively separate the electrons and holes, and inhibit the recombination of photon-generated carriers, thereby increasing the photocatalytic efficiency. Second, exfoliated montmorillonite is added to the reactants, and as a result, Bi_2SiO_5 and $\beta-Bi_2O_3$ are in-situ formed simultaneously. The utilization of light is improved due to the larger light response range of $\beta-Bi_2O_3$. Third, the negative charge electrostatic interaction on the surface of EB can accelerate the separation of electrons and holes and inhibit the recombination of electron-hole pairs. Furthermore, $Bi_2SiO_5/Bi_2O_3/EB$ has a higher specific surface area than bare $\alpha-Bi_2O_3$ and has a stronger adsorption for RhB. Thus, the active species produced by light irradiation are more likely to oxidize the contaminants adsorbed on the catalyst surface.

According to the discussion above, a possible mechanism of the RhB photodegradation by $Bi_2SiO_5/Bi_2O_3/EB$ photocatalysts was proposed (see Fig. 11). According to the equation $E_{NHE} = E_{Ag/AgCl} + E^0_{Ag/AgCl}$ (0.197 6 V) and $E_{VB} = E_{CB} + E_g$, the valence band positions of $\alpha-Bi_2O_3$, $\beta-Bi_2O_3$ and Bi_2SiO_5 are estimated to be 3.07 eV, 2.62 eV and 3.52 eV, respectively. The conduction band positions of $\alpha-Bi_2O_3$, $\beta-Bi_2O_3$ and Bi_2SiO_5 are estimated to be 0.33 eV, 0.27 eV and -0.06 eV, respectively^[27, 29, 55–56]. The band edges of $\beta-Bi_2O_3$ and Bi_2SiO_5 exhibit a typical embedded structure, which may be unfavorable for the transport of photogenerated electrons and holes. However, when the n-type Bi_2SiO_5 and p-type $\beta-Bi_2O_3$ are mutually contacted, a p-n heterogenous junction can be constituted on the interface of Bi_2SiO_5 and $\beta-Bi_2O_3$ ^[57–58]. In addition, when Bi_2SiO_5 and $\beta-Bi_2O_3$ are in contact with each other, the photogenerated carriers on the interface of the two semiconductors are redistributed to reach an equilibrium of the Fermi energy (E_f), and the Fermi levels of the two

semiconductors eventually converge to be uniform^[59–61]. Therefore, an internal electric field can be established in Bi_2SiO_5 and $\beta\text{-Bi}_2\text{O}_3$ composite, and the positive and negative charges can be accumulated on Bi_2SiO_5 and $\beta\text{-Bi}_2\text{O}_3$, separately. Simultaneously, the position of conduction band and valence band is altered at the Fermi level. As the Fermi level is uniform, the band position of Bi_2SiO_5 moves to the positive position, while $\beta\text{-Bi}_2\text{O}_3$ moves to the negative position. Thus, under the solar

light irradiation, the electrons on $\beta\text{-Bi}_2\text{O}_3$ conductive band can be easily transferred to the CB of Bi_2SiO_5 , reacting with O_2 to produce $\cdot\text{O}_2^-$. $\cdot\text{O}_2^-$ is an active species with a strong oxidizing ability and can react with RhB. Conversely, h^+ on the Bi_2SiO_5 valence band can be easily transferred to the VB of $\beta\text{-Bi}_2\text{O}_3$, and then directly reacted with RhB, which allows the electrons and holes to separate more efficiently and reduce the carrier recombination, thus enhancing the photocatalytic efficiency.

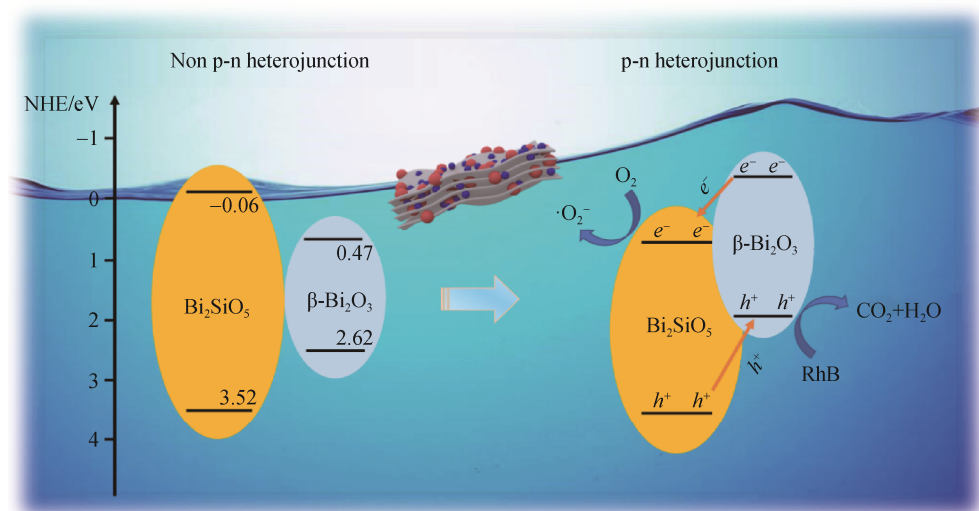


Fig. 11 Possible photodegradation mechanism of RhB by $\text{Bi}_2\text{SiO}_5/\text{Bi}_2\text{O}_3/\text{EB}$ photocatalysts under a simulated solar light irradiation

4 Conclusions

$\text{Bi}_2\text{O}_3/\text{Bi}_2\text{SiO}_5$ p-n heterojunction was *in-situ* synthesized on exfoliated montmorillonite *via* a novel one-pot method. The as-prepared $\text{Bi}_2\text{O}_3/\text{Bi}_2\text{SiO}_5/\text{EB}$ sample had the superior photocatalytic performance and stability in the RhB degradation under simulated sunlight irradiation, exhibiting a maximum removal efficiency of 96.89%, which was 49 times greater than that of bare $\alpha\text{-Bi}_2\text{O}_3$. The increased photocatalytic performance was contributed to the larger specific surface area, stronger adsorption capacity, creation of $\beta\text{-Bi}_2\text{O}_3$ and fabrication of $\beta\text{-Bi}_2\text{O}_3/\text{Bi}_2\text{SiO}_5$ heterojunction. This study presented a principal route to fabricate the efficient bismuth-based photocatalysts for the RhB degradation.

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