Photoelectrochemical and Photo-Fenton Mechanism of Enhanced Visible Light-Driven Nanocatalyst Synthesis of ZnFe₂O₄/BiOI

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Abstract

Based on the fact that the photo-Fenton process can directly use solar energy to degrade various pollutants, it has received widespread attention. However, it has attracted widespread attention due to the rapid recombination of photo-generated carriers and the low light response range. Therefore, the construction of a Z-scheme heterojunction in this paper can effectively enhance the electron-hole separation, increase the reduction and oxidation potential, and enhance the redox capability of the photocatalyst. This paper reports the successful preparation of visible-light-induced $\text{ZnFe}_2\text{O}_4/\text{BiOI}$ composite photocatalyst. There is a Z-scheme heterojunction structure of ZnFe_2O_4 and BiOI. At the same time, the PL and UV absorption spectra showed that the light absorption performance of the composite nanomaterials was enhanced, the photo-generated carriers recombination rate was reduced, and the photo-Fenton performance was also significantly improved. And the photocurrent of $\text{ZnFe}_2\text{O}_4/\text{BiOI}$ is more than 29 times that of pure ZnFe_2O_4 . In addition, $\text{ZnFe}_2\text{O}_4/\text{BiOI}$ can degrade the simulated pollutant RhB 100% within 20 min under simulated sunlight. It shows that $\text{ZnFe}_2\text{O}_4/\text{BiOI}$ binary composite has excellent photo-Fenton properties. In addition, $\text{ZnFe}_2\text{O}_4/\text{BiOI}$ still maintains a high photo-Fenton ability after three cycles. Therefore, it has potential application prospects of the industrial photodegradation of organic pollutants.

1. Introduction

In recent decades, with the rapid development of global industrialization and the large-scale application of organic dyes, the shortage of freshwater resources and water pollution have become a global problem facing human society. It has attracted significant attention to scholars at home and abroad. (Chen et al. 2018, Hasija et al. 2019, Hu et al. 2019, Sharma & Feng 2019, Yang et al. 2020) Traditional semiconductor photocatalysts (such as TiO_2 and ZnO) can only respond to ultraviolet light and have low utilization in the visible light band; photo-generated electron-hole pairs are elementary to recombine, and the photocatalytic efficiency is low; powdered catalysis are challenging to separate from the reaction solution, it will cause the loss of motivation and secondary pollution of the water. (Guo et al. 2019a, Guo et al. 2019b, Meng et al. 2019, Wu et al. 2020, Yendrapati et al. 2020, Zhou et al. 2020b) Therefore, it is urgent to develop more superior water treatment technologies to solve these problems and realize the sustainable development of human society. The researchers have combined the advantages of iron-based oxide photocatalysis technology and Fenton oxidation technology to realize the cycle of the photo-Fenton process, which makes the system produce more $\cdot\text{OH}$ with solid oxidizing ability, thereby enhancing the degradation of pollutants in wastewater effectiveness. (Clarizia et al. 2017, Mirzaei et al. 2017, Xing et al. 2018) Photo-Fenton technology has unique advantages such as low preparation cost, fast degradation rate and less secondary pollution. It has shown broad application prospects of the use of solar energy to degrade pollutants. (Huang et al. 2017, Liu et al. 2017, Zhang et al. 2019)

The spinel structures metal oxide belongs to the cubic crystal system, and its general formula is AB_2O_4 . The A position represents the tetrahedral position occupied by the divalent metal ion. The tetrahedral gap

is surrounded by four oxygen ions; the B position means the octahedral position occupied by the trivalent metal ion octahedral void is surrounded by six oxygen ions.(Behera et al. 2019, Jiang et al. 2018, Zhou et al. 2020a) Spinel structure ZnFe_2O_4 has the characteristics of non-toxic, stable chemical properties, photochemical corrosion resistance, simple preparation and low cost.(Cai et al. 2016, Chen et al. 2021, Xiang et al. 2020) Compared with traditional photocatalysts, ZnFe_2O_4 has a narrower bandgap, is more sensitive to visible light, has a broader spectral response range, and has good photocatalytic activity. (Chen et al. 2010, Zheng et al. 2020)

This paper reports the preparation of spinel structure ZnFe_2O_4 by hydrothermal method and the construction of $\text{ZnFe}_2\text{O}_4/\text{BiOI}$ Z-scheme hetero-junction degradation dyed RhB. Compared with ZnFe_2O_4 , the photo-Fenton degradation reaction rate of $\text{ZnFe}_2\text{O}_4/\text{BiOI}$ is 27 times higher than that of ZnFe_2O_4 , and the reaction rate of $\text{ZnFe}_2\text{O}_4/\text{BiOI}$ photo-Fenton degradation RhB is 19 times higher than that of $\text{ZnFe}_2\text{O}_4/\text{BiOI}$ photocatalytic degradation rate. The origin of photo-Fenton activity improvement is explored to study of structure, morphology, optics and electrochemistry. The main reaction species in the visual Fenton process is the use of various chemical scavengers for research. After three cycles of reaction, the degradation rate of RhB remained at 81.6%.

2. Experimental Procedures

2.1. Synthesis of $\text{ZnFe}_2\text{O}_4/\text{BiOI}$ heterojunction

Weigh 0.05 mol of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 0.1 mol of $\text{Fe}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, respectively, and dissolve them in 40mL of deionized water, sonicate for 15 min and stir for 30 min. Next, adjust the pH to 13 and pass the 6M NaOH solution, transfer the mixture to a 100 mL stainless steel autoclave lined with PTFE, and react at 180°C for 24 h. After the samples were cooled to room temperature, they were washed alternately with deionized water and ethanol three times and then placed in an oven at 60°C for 8 h. Then the mixture is annealed at 500 °C for 5 h to obtain zinc ferrite powder, represented by ZnFe_2O_4 (abbreviated as ZFO). Weigh 0.05 mol ZnFe_2O_4 and 0.1 mol $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ respectively and dissolve them in absolute ethanol. Next, dissolve 0.05 mol KI in deionized water and stir until the drug is completely dissolved; Add the KI solution dropwise to $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$. Adjust the solution to pH=7, stir for 30 min, transfer to a 100 mL stainless steel autoclave lined with PTFE, and keep at 100°C for 12 h. After the sample is cooled to room temperature, wash with deionized water and ethanol alternately three times. Put it in an oven at 60 °C and dry it for 8 h to obtain the composite powder $\text{ZnFe}_2\text{O}_4/\text{BiOI}$. By changing the molar ratio of ZnFe_2O_4 and BiOI to 1:1, 1:2 and 1:3, a composite photocatalyst was prepared and named ZFO / BOI -1, ZFO / BOI -2, ZFO / BOI -3. For comparison, pure BiOI (abbreviated as BOI) has also synthesized via the same method without the addition of ZnFe_2O_4 .

2.2. Characterization

X-ray diffractometer (Rigaku, Japan, D/Max-2400 type, Cu K α radiation, $\lambda = 1.54056 \text{ \AA}$, scanning range of 10-90 °, step length of 0.02 °) was used to analyze the phase structure of the samples. The microscopic morphology and particle size of the materials were observed by scanning electron microscope (SEM, JSM-6701F) and high-resolution transmission electron microscope (HRTEM, JEM-1200EX). The UV-Vis diffuse reflectance spectra (UV-Vis DRS, PERSEE TU-1901) of photocatalysts were recorded by a double-beam UV-Vis spectrophotometer, using BaSO₄ as the reference material (scan interval: 200-850 nm, step size: 0.5 nm). The multifunctional X-ray photoelectron spectrometer (XPS, AXIS SUPRA) was used to analyze the chemical element valence state of the materials. Analyze the surface area and pore size distribution of samples using the Specific Surface and Porosity Analyzer (ASAP Model 2020). The photoluminescence (PL) spectrum of the photocatalyst was recorded by a fluorescence phosphorescence luminescence spectrophotometer (LS-55) with an excitation wavelength of 325 nm. The Fourier transform infrared spectra (FT-IR) of the samples were tested by an infrared spectrometer (Spectrum Two) in the range of 500~4000 cm⁻¹ using KBr as the background.

2.3. Photo-electrochemical measurement

Electrochemical impedance spectra (EIS), transient photocurrent response and Mott-Schottky (M-S) curves of ZnFe₂O₄/BiOI composite photocatalysts were measured in Na₂SO₄ (0.1 M) solution by an electrochemical workstation (CorrTest, CS350) with a typical three-electrode electrolytic cell. A saturated calomel electrode (SCE) was used for the reference electrode. 8 mg photocatalyst and 1 mg acetylene black were ground and mixed evenly, 1-methyl-2-pyrrolidone (NMP) was used as dispersant and polyvinylidene fluoride (PVDF) was used as binder, which were dropped and stirred in turn, and then coated on the surface of conductive glass. After drying at 60 °C, the working electrode was obtained. The electrochemical impedance spectra were measured at a sinusoidal voltage signal of 5 mV in the frequency range of 10⁻² to 10⁵ Hz. The transient photocurrents (I-t curves) were measured at fixed bias potential of 0.2 V. The Mott-Schottky (M-S) curves were measured at 3000 and 5000 Hz in 0.1 M Na₂SO₄.

2.4. photo-Fenton experiment

Rhodamine B was degraded under simulated sunlight under xenon lamp irradiation to test the photo-Fenton performance. The initial concentration was 5 mg/L, and the photocatalytic degradation experiment used 100 mL of RhB. Before the xenon lamp irradiation, stir the suspension for 0.5 h in the dark to reach the adsorption/desorption equilibrium of the photocatalyst surface. Take a small amount of solution every 15 min to measure the concentration of RhB during the photocatalytic degradation process. Since photo Fenton has a significant effect in degrading pollutants, the initial concentration of RhB in the photo Fenton degradation experiment is 10 mg/L. The photo-Fenton experiment uses 100 mL RhB, the initial concentration is 10 mg/L, and the photocatalyst is 0.01 g. Adjust the initial pH of the dye solution by using 0.1 M sulfuric acid and 0.1 M sodium hydroxide. At the same time, the catalyst was added to the RhB solution, and stirring was continued for 30 min to reach the absorption-desorption equilibrium. Subsequently, H₂O₂ was added, and visible light was irradiated on the suspension immediately. Take out a small amount of solution every 5 min to measure the concentration of RhB. Use

a visible spectrophotometer ($\lambda = 554 \text{ nm}$) to test the absorbance of the solution. The Lambert-Beer law defines the degradation rate: $(C_t - C_0)/C_0 \times 100\% = (A_0 - A_t)/A_0 \times 100\%$, where C_0 represents the initial solution concentration, C_t represents the concentration of the solution after time t . After exposure time t , A_0 and A_t respectively is the corresponding absorbance of the solution. In the active species capture experiment (BQ), p-benzoquinone, ethylenediaminetetraacetic acid (EDTA) and isopropanol (IPA) were used as capture agents for $\cdot\text{O}_2^-$, h^+ and $\cdot\text{OH}$ respectively.

3. Results And Discussion

3.1. XRD and morphology analysis

Through X-ray diffraction (XRD) analysis, the pure ZFO sample showed 5 obvious characteristic diffraction peaks at $2\theta = 29.9, 35.2, 42.8, 56.6$ and 62.1° , corresponding to ZFO (2 2 0), (3 1 1), (1 0 0), (5 1 1) and (4 4 0) crystal planes, which coincide with the diffraction peak positions of the ZFO JCPDS standard card (79-1150). The pure BOI sample has 5 distinct characteristic diffraction peaks at $2\theta = 29.7, 31.7, 45.5, 51.5$ and 55.3° , corresponding to BOI (012), (110), (020), (114) and (122) crystal planes, which coincide with the diffraction peak positions of the BOI JCPDS standard card (PDF#73-2062). The X-ray diffraction pattern of ZFO/BOI composite material shows that in addition to the significant diffraction peaks of BOI, there are also ZFO diffraction peaks, and no impurity phase is observed, which indicates that ZFO and BOI have been successfully recombined.

Figure 2a shows the SEM image of pure ZFO. The hydrothermally synthesized ZFO has a uniform spherical structure. Fig. 2d is the SEM image of the composite ZFO/BOI-2. It can be seen that the composite material is a flake BOI with uniformly attached ZFO pellets. Fig. 2b shows the TEM image of the ZFO/BOI-2 sample. The structure composed of flakes and small balls can be observed, consistent with the SEM image of ZFO/BOI. It can be seen from the mark in Fig. 2c that the enlarged view of the circular area is Fig. 2f, and its lattice spacing is 0.25 nm, which corresponds to the (311) crystal plane of ZFO. The enlarged view of the square area in Fig. 2c is Fig. 2g, and its lattice spacing is 0.28 nm, which corresponds to the (110) crystal plane of BOI. Fig. 2e is a selected area of electron diffraction (SAED), showing a diffraction ring composed of many homogeneous and tiny crystals. The cyan diffraction rings represent the (2 2 0), (3 1 1), (5 1 1) and (4 4 0) crystal planes of ZFO crystals, and the yellow diffraction rings represent the (012), (1 1 0), (0 2 0) and (1 2 2) crystal planes, consistent with the XRD results. The above results indicate the existence of binary composite ZFO/BOI. At the same time, there is a close relationship between ZFO and BOI, forming a Z-scheme heterojunction, which is advantageous for separating photogenerated carriers.

Figure 3 shows the result of using the EDS test to determine the element types in the composite ZFO/BOI. Fig. 3b-f can be seen the five elements of O, Zn, Fe, Bi and I in the composite. It is not difficult to find from the EDS element distribution diagram that the distribution of each element is consistent with the shape of the composite material, which further proves that the composite material ZFO/BOI was successfully prepared without other impurities.

3.2. XPS and N₂ adsorption–desorption

We use XPS to study the elemental composition and chemical valence of ZFO/BOI-2 nanocomposites. Fig. 4 detects the peak signals of the six elements C, Zn, Fe, Bi, O and I in the ZFO/BOI-2 nanocomposite. The C1s spectrum (Fig. 4a) fits three peaks at 585.3, 586.8 and 589.2 eV, respectively, which indicates that the carbon species in this sample has three different chemical environments. The binding energy (BE) of 285.3 eV coincides with -C-C and is identified as graphite or adventitious carbon. The peak at 286.8 eV is designated to be embedded in the C-O bond in the interlayer compound. The peak close to 289.2 eV indicates the presence of carbonate species (C=O). (Zeng et al. 2019) The peaks at 1045.2 and 1021.9 eV in Fig. 4b can be designated as the binding energies of Zn 2p_{1/2} and Zn 2p_{3/2}, which are similar to the standard data of Zn²⁺. (Li et al. 2011) In the Fe 2p spectrum from 740 to 705 eV (Fig. 4c), the two prominent peaks belonging to Fe 2p_{1/2} and Fe 2p_{3/2} appear at 725.8 and 711.9 eV, while the satellite peak of Fe 2p_{3/2} is at 720 eV. The binding energy of Fe 2p_{2/3} is 710.9 eV, which matches the binding energy of Fe 2p_{2/3} in ZFO very well. Meanwhile, Fe 2p_{3/2} peaks can be deconvoluted into two peaks located at 711.9 and 710.9 eV, allocated to octahedral and tetrahedral Fe³⁺, respectively. (Cai et al. 2016, Li et al. 2018b) According to Fig. 4d, the two typical peaks of Bi 4f are located at 159.6 and 164.9 eV, and respectively, this finding confirmed that Bi³⁺ cations in ZFO/BOI composites correspond to Bi 4f_{5/2} and Bi 4f_{7/2}, respectively. (Qiu et al. 2017, Yang et al. 2018) The O1s map (Fig. 4e) fitted three peaks at 530.2, 531.5 and 532.8 eV respectively. The characteristic peak at 530.2 eV was derived from the Bi-O bond of {Bi₂O₂}²⁺ layer in BOI, and the peak at 531.9 eV was corresponding to the Fe-O bond in ZFO. The peak at 532.8 eV corresponds to the characteristic peak of free oxygen or hydrated oxides on the sample surface. (Bai et al. 2019, Tian et al. 2020) Two peaks were observed at about 619.5 and 631 eV corresponding to I 3d_{5/2} and I 3d_{3/2}, respectively (Fig. 4f), which were attributable to the I⁻ ion of BOI. (Li et al. 2018a) In addition, the above analysis indicated the presence of BOI and ZFO in the composite sample.

The specific surface area and pore size distribution of pure ZFO and ZFO/BOI-2 composites were studied by speed ratio surface and porosity analyzer. As shown in Fig. 5a, the nitrogen adsorption-desorption isotherms of pure ZFO and ZFO/BOI-2 photocatalysts are in the range of 0-1.0 P/P₀, and there is an evident IV type H₃ hysteric ring. The IV type H₃ hysteric ring indicates that the sample has a mesoporous structure and is composed of flake nanoparticles, (Raza & Faraz 2020) which is consistent with SEM and HRTEM. In addition, the specific surface areas of pure ZFO and ZFO/BOI-2 were 88.988 and 42.538 m²/g, respectively, calculated by Brunauer-Emmett-Teller (BET) model. The corresponding pore size distribution of the samples was determined by the BJH method, and the average adsorption pore size of ZFO and ZFO/BOI-2 was 151.06 and 218.39 Å.

3.3. Optical analysis

The light absorption capacity of semiconductor materials has an important influence on the photocatalytic activity. We analyzed the spectral absorption range of the photocatalyst by UV-Vis

absorption spectrum. Fig. 6 shows the UV-Vis absorption spectra of the nanomaterials in the 250-800 nm range. Compared with pure BOI samples, the absorption intensity of ZFO/BOI samples was significantly improved in the range of 600-800 nm, and the absorption edge was redshifted. This indicates that the binary composite photocatalyst can enhance the response in the visible region. According to Fig. 6b, the E_g values of ZFO and BOI were 1.71 and 2.02 eV, respectively. The red shift of the Z-scheme heterojunction ZFO/BOI may be due to the synergy between the flake BOI and ZFO nanoparticles.

PL spectroscopy is an effective method to study the composite behaviour of photo charges generated by photocatalyst. The PL spectra of pure ZFO and ZFO/BOI nanocomposites are shown in Fig. 7. Pure ZFO and ZFO/BOI nanocomposites show a luminescence peak at 505 nm. The luminescence intensity of ZFO/BOI nanocomposites is lower than that of pure ZFO, and the luminescence peak intensity of ZFO/BOI-2 is the lowest. The recombination rate of photogenerated carriers is the lowest. ZFO nanoparticles were modified on the surface of the flake BOI nanostructures to construct the ZFO/BOI heterojunction and the recombination rate of photogenerated carriers could be effectively reduced. However, when the content of BOI in ZFO/BOI is too high, many electron-hole pairs will recombine on the surface of BOI.

As shown in Fig. 8, the characteristic peaks located at 3445 cm^{-1} and 1626 cm^{-1} are respectively the O-H bond stretching vibration peaks and H-O-H. (Yosefi et al. 2017) In addition, the vibration mode corresponding to CH_3 -bending was detected at 1383 cm^{-1} . (Tamaddon et al. 2020) For pure BOI, the absorption peak located at 500 cm^{-1} is derived from the stretching vibration of the Bi-O bond. (Zhou et al. 2017) In addition, for the spinel ZFO sample, the A position is mainly occupied by Zn^{2+} , and Fe^{3+} mainly occupies the B position. The characteristic peaks located at 571 cm^{-1} and 418 cm^{-1} correspond to the stretching vibrations of the Zn-O and Fe-O bonds in the tetrahedral and octahedral positions, respectively. (Khasevani & Gholami 2019)

3.4. photo electrochemical properties analysis

The CB and VB potentials of ZFO and BOI were determined by Mott-Schottky (M-S) plots. By extrapolating the linear part of the M-S plots to the horizontal axis. The slope of the M-S plot of ZFO is positive, indicating that it is an n-type semiconductor. That of BOI is negative, showing as a p-type semiconductor. According to $V(\text{NHE})=V(\text{SCE})+0.059\text{pH}+0.242(\text{pH}=7)$, (Huang et al. 2021) the relative standard calomel electrode (vs SCE) potential is converted to the standard hydrogen electrode (vs NHE) potential. It can be seen from Fig. 9a that the $V(\text{SCE})$ of ZFO is -1.21 V, the $V(\text{SCE})$ of BOI is 1.07 V. It is generally believed that the VB edge potential of p-type semiconductors and the CB edge potential of n-type semiconductors can be approximately equal to the VFB of semiconductors. Since ZFO is an n-type semiconductor, the conduction band potential of ZFO is $V_{\text{CB}}=V(\text{NHE})=-0.55\text{ V}$. The valence band potential of BOI is $V_{\text{VB}}=V(\text{NHE})=1.72\text{ V}$ because BOI is a p-type semiconductor.

EIS impedance spectroscopy and transient photocurrent test research were carried out to understand the photo-Fenton mechanism in-depth. Fig. 10a shows that the EIS of nanomaterials is approximately

semicircle in the high-frequency region. The semicircle diameter of ZFO/BOI composite in the high-frequency region is smaller than that of pure ZFO and BOI, which indicates that it has a low charge transfer resistance. The results show that the ZFO/BOI heterojunction can significantly improve photogenerated electron-hole pairs' separation and migration efficiency. Fig. 10b shows the transient photocurrent response of the sample in five cycles of on/off under simulated sunlight. The photocurrent densities of ZFO, BOI, ZFO/BOI-1, ZFO/BOI-2 and ZFO/BOI-3 photocatalysts were 5.82×10^{-8} , 1.34×10^{-7} , 1.27×10^{-6} , 1.71×10^{-6} and 6.5×10^{-7} mA/cm², respectively. After the light is turned off, the photocurrent is reduced to the initial value. Compared with pure ZFO and BOI, the photocurrent density of ZFO/BOI-2 heterojunction is significantly increased, indicating that the photogenerated carriers of ZFO/BOI-2 heterojunction can be separated and migrated more effectively. By comparing the EIS and transient photocurrent responses of pure and composite photocatalysts, the ZFO/BOI nanocomposites showed better-photogenerated charge separation and migration ability, which indicated that the ZFO/BOI heterojunction composite photocatalyst might have better Fenton activity.

3.5. Photo-Fenton analysis

The photo-Fenton activity of ZFO/BOI heterojunction was tested by dissolving RhB in simulated solar degradation. Fig. 11a shows the degradation rates of photo-Fenton degradation of RhB by pure ZFO, BOI and ZFO/BOI nanocomposites with different composite ratios. Under the action of photocatalytic degradation, the concentration of RhB dye decreases with the increase of the illumination time. Under the illumination condition of 90 min, ZFO, BOI, ZFO/BOI-1, ZFO/BOI-2 and ZFO/BOI-3 nanocomposites had degradation rates of 27.5, 58.9, 84.1, 88.6 and 78.1%, respectively. In Fig. 11c, the degradation rates of ZFO, BOI, ZFO/BOI-1, ZFO/BOI-2 and ZFO/BOI-3 nanocomposites were 24.3, 51.9, 96.9, 100 and 94.6%, respectively, under the light condition of only 20 min. The photo-Fenton degradation rate of ZFO/BOI heterojunction was significantly higher than that of pure ZFO and BOI, and the photo-Fenton activity of ZFO/BOI-2 was the strongest. The excellent photonic Fenton properties of ZFO/BOI nanocomposites are since highly dispersed ZFO particles are uniformly distributed on the surface of the sheets of BOI and fully contact to form a ZFO/BOI heterojunction. ZFO/BOI heterojunction can enhance the visible light absorption capacity. Moreover, this novel ZFO/BOI heterojunction can promote the migration and separation of photogenerated carriers and inhibit their recombination, thus improving the photo-Fenton degradation ability. Through the first-order kinetic model equation: $\ln(C_t/C_0) = -K_{app}t$, the kinetics characteristics of the degradation of RhB by ZFO/BOI heterojunction photo-Fenton can be quantitatively studied, where K_{app} is the first-order kinetic reaction rate, and C is the concentration of RhB dye. Fig. 11b is ZFO/BOI photocatalytic degradation of corresponding first-order kinetics curves of ZFO, BOI, ZFO/BOI-1, and ZFO/BOI-2, ZFO/BOI-3 samples of the reaction rate constant K_{app} were 0.0025, 0.0083, 0.016, 0.021 and 0.015 min⁻¹. Fig. 11d is Fenton ZFO/BOI light degradation of corresponding first-order kinetics curve, ZFO, BOI, ZFO/BOI-1, ZFO/BOI-2, and ZFO/BOI-3 samples of the reaction rate constant K_{app} were 0.0147, 0.0857, 0.1518, 0.4008 and 0.1404 min⁻¹. The K_{app} value of ZFO/BOI-2 was the highest in the composite sample, indicating that the photo-Fenton degradation rate of ZFO/BOI-2 was the highest, and the photo-Fenton degradation rate was about 19 times that of the photocatalytic degradation rate. As the

amount of BOI increases, K_{app} first increases and then decreases. A part of photogenerated carriers will recombine on the BOI surface because when the BOI content in ZFO/BOI is too high.

Test the active species of ZFO/BOI-2 photo-Fenton to degrade RhB through the dynamic species capture experiment, using ethylenediaminetetraacetic acid (EDTA), p-benzoquinone (BQ) and isopropyl alcohol (IPA) to capture h^+ , $\cdot O_2^-$ and $\cdot OH$. The illustration in Fig. 12 shows the degradation of RhB over time in the ZFO/BOI-2 sample after adding different capture agents. The degradation rate decreased when EDTA or BQ was added. The photocatalytic degradation rate of ZFO/BOI-2 samples decreased significantly after adding IPA, indicating that shows that $\cdot OH$ is the main active substance. The role of $\cdot O_2^-$ and h^+ in the degradation of photo-Fenton is relatively weak.

Repeated cyclic tests investigated the stability of ZFO/BOI-2 nanomaterials under the same environment. In Fig. 13, the first degradation rate of the catalyst was 100% after 25 min. Although the degradation rate decreases slightly with the number of cycles, the degradation rate can still reach 81.6% after three cycles, indicating that the cycling stability of ZFO/BOI-2 composite material is good. The ZFO/BOI photocatalyst can be recovered by an external magnetic field due to the ferromagnetic nature of ZFO. ZFO/BOI photocatalyst shows good stability and reproducibility in RhB degradation, which can be used in the actual dye wastewater purification.

3.6. Possible mechanism

It is proposed that the carrier migration mode of Z-scheme heterojunction ZFO/BOI (Fig. 14) is generated because BOI and ZFO absorb enough energy photons to excite electron transition from the valence band to the conduction band. The valence band and conduction band of BOI are lower than that of ZFO, and the photoelectrons in the conduction band of BOI can migrate to the valence band of ZFO to recombine with h^+ . The remaining carriers undergo redox reactions in the valence band of ZFO and the conduction band of BOI, respectively. In the process of photo-Fenton degradation, e^- of ZFO conduction band reacts with O_2 in water to generate $\cdot O_2^-$. In addition, because of the strong oxidation of h^+ , part of it can directly degrade RhB, a small part h^+ can react with OH^- to form $\cdot OH$. The simplified possible reaction of generating hydroxyl radicals in the process of adding hydrogen peroxide to the acidic solution is determined by r_1 and r_2 , as shown below:

$\cdot O_2^-$, h^+ and $\cdot OH$ radicals produced in the photo-Fenton reaction degrades RhB dye into H_2O , CO_2 and small molecule substances. This is consistent with the above capture experiment results. Therefore, Z-scheme heterojunction ZFO/BOI construction has a noticeable effect on inhibiting the recombination of photo-generated charges and can also improve carriers' transport and separation efficiency. The photo-Fenton process helps to strengthen its economic and environmental sustainability.

4. Conclusions

A series of magnetically separable Z-type heterojunction composite materials with different BOI content were successfully prepared by hydrothermal and subsequent co-precipitation methods. The prepared catalyst shows excellent degradation performance and sufficient magnetic properties for the degradation of RhB under simulated sunlight irradiation. It can be reused in the photo-Fenton process, especially ZFO/BOI-2. Optical analysis and photoelectrochemical analysis indicate that the improved RhB removal efficiency of ZFO/BOI-2 may be attributed to the synergy between ZnFe_2O_4 and BiOI, which may lead to effective electron-hole pair separation. The trapping experiment results show that $\cdot\text{OH}$ radicals are the main reaction substances that promote the oxidation and reduction of the photo-Fenton process. This work can understand the process of using magnetic catalysts to degrade pollutants under sunlight.

Declarations

Ethics approval Not applicable.

Consent to participate Not applicable.

Consent for publication All authors agree to publish.

Availability of data and materials Not applicable.

Competing interests The authors declare no competing interests.

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Authors' contributions Chao Li provides conceptualization, methodology, software, review, editing and verification. Zhiqiang Wei analyzed and explained the relevant photo-Fenton data. Qiang Lu provides some tests. Jinhuan Ma and Ling Li provide some ideas in writing the manuscript. Final manuscript read and approved by all authors.

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Figures

Figure 1

XRD patterns of ZFO, BOI and ZFO/BOI composites

Figure 2

SEM images of (a) ZFO, (d) ZFO/BOI-2 and (b) TEM image and (c, f, g) HRTEM images and (e) SAED pattern of ZFO/BOI-2 composites

Figure 3

EDS elemental mapping images of ZFO/BOI-2 composites

Figure 4

XPS spectrometer of ZFO/BOI-2 composites (a) C 1s, (b) Zn 2P, (c) Fe 2p, (d) Bi 4f, (e) O 1s and (f) I 3d

Figure 5

(a) Nitrogen adsorption-desorption isotherms and (b) pore size distribution of ZFO and ZFO/BOI-2 composites

Figure 6

(a) UV-vis DRS spectra of ZFO, BOI and ZFO/BOI samples, (b) $(\alpha h\nu)^{1/2}$ vs $h\nu$ curves

Figure 7

PL spectra of pure ZFO and ZFO/BOI -2 composites

Figure 8

FT-IR spectroscopy of ZFO, BOI and ZFO/BOI -2 samples

Figure 9

M-S plots of (a) ZFO and (b) BOI samples

Figure 10

(a) Electrochemical impedance spectroscopy Nyquist plots and (b) transient photocurrent responses of pure ZFO, BOI and ZFO/BOI -2 samples

Figure 11

(a) The photocatalytic and (c) the Photo-Fenton degradation of RhB over time and (b) The photocatalytic and (d) the Photo-Fenton plots of $\ln(C_t/C_0)$ vs. irradiation time for pure ZFO, BOI and ZFO/BOI samples

Figure 12

Photocatalytic degradation of ZFO/BOI-2 samples with different trapping agents

Figure 13

Recyclability of ZFO/BOI -2 for photocatalytic degradation of RhB

Figure 14

The schematic diagram of photocatalytic mechanism of the ZFO/BOI composites under simulated sunlight