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Effect of *in situ* Fe(II)/Fe(III)-doping on the visible light-Fenton-like catalytic activity of Bi/BiOBr hierarchical microspheres†

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Novel Fe(II)/Fe(III) doped Bi/BiOBr (FBB) visible light photocatalysts with heterojunctions were successfully prepared by a facile solvothermal method. The as-prepared samples were characterized *via* XRD, FESEM, XPS, UV-vis absorption spectroscopy and N₂ adsorption-desorption. The results demonstrate that Fe doping plays key roles in the transformation of amorphous to crystal phase for Bi metal nanoparticles and the increase of specific surface areas for FBB. The degradation of rhodamine B (RhB) was studied using FBB with hydrogen peroxide (H₂O₂) under visible light irradiation ($\lambda = 420$ nm); it was found that the degradation rate constant for 0.2-FBB (Fe/Bi molar ratio = 0.2) is 4-fold more than that for pure BiOBr. The presence of visible light enhances the Fenton-like reaction by the reduction of $\equiv\text{Fe(III)}$ to $\equiv\text{Fe(II)}$, producing more holes and hydroxyl radicals to degrade RhB. This result is confirmed by ESR spectroscopy, H₂O₂ consumption and surface Fe(II) concentration experiments. Radical scavenger experiments demonstrated that the active species follow the order holes > hydroxyl radicals. After five cycles, 0.2-FBB retains stable catalytic activity.

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1. Introduction

Safe drinking water is essential for a life of health. With the rise of new, toxic and persistent contaminants from human activities, conventional treatment methods cannot meet the potable water standards that people demand.^{1–3} Fortunately, advanced oxidation processes (AOPs) have been applied for the treatment of drinking water and wastewater containing new pollutants. AOPs employ chemical oxidants (hydrogen peroxide (H₂O₂), persulfate, and ozone) and photochemical and sonochemical techniques to generate reactive species (*i.e.* hydroxyl, superoxide, and sulfate radicals). Hydroxyl radicals from the Fenton-like reaction are environmentally-friendly and have a higher redox potential (2.8 eV),⁴ the production of which is summarized as follows:

The generation of hydroxyl radicals is attributed to iron-catalyzed decomposition of H₂O₂ (eqn (1)), and then the reduction of $\equiv\text{Fe(III)}$ with H₂O₂ regenerates $\equiv\text{Fe(II)}$ (eqn (2)), producing a propagating reaction.^{5,6} However, the reduction of $\equiv\text{Fe(III)}$ to $\equiv\text{Fe(II)}$ is the rate-limiting step in the overall reaction, because the reaction of $\equiv\text{Fe(III)}$ with H₂O₂ is much slower than that of $\equiv\text{Fe(II)}$. Light irradiation could facilitate the reduction of $\equiv\text{Fe(III)}$ (eqn (3)) in order to improve the degradation efficiency of pollutants.^{7–11}

Bismuth oxide bromide (BiOBr), as a photocatalyst under visible light, has attracted great interest owing to its high photocatalytic activity and stability.¹² BiOBr possesses a tetragonal matlockite and layered structure, which is characterized by [Bi₂O₂] slabs interleaved with double slabs of bromine atoms. However, the band gap of BiOBr was about 2.9 eV,¹³ absorbing only a part of visible light. To overcome this drawback, many methods were adopted, including various hierarchical nanostructures^{14,15} and halogen-mixing solid solutions.^{16,17} In addition, transition metal modification can enhance the photocatalytic activity of BiOBr. Recent research on transition metal (Zn, Sn) modification of BiOBr has exhibited that this way can result in a higher photocatalytic activity,^{13,18} but metal oxides on the surface can readily decrease their photocatalytic activities. The presence of H₂O₂ and light can activate the catalytic active sites to improve their activity, so we introduced Fe(II)/Fe(III) into the BiOBr

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lattice to enhance the photocatalytic efficiency in the presence of H_2O_2 .

In this paper, we prepared a series of Fe(II)/Fe(III) doped Bi/BiOBr by a solvothermal method for the first time. The resultant products were characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), field emission scanning electron microscopy (FESEM), UV-vis diffuse reflectance spectroscopy (DRS), and Brunauer–Emmett–Teller specific surface area (BET). In addition, the introduction of hydrogen peroxide (H_2O_2) can significantly improve the photocatalytic activity.

2. Experimental section

2.1 Materials

Bismuth nitrate pentahydrate ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, 98%), ferrous chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, 99%), potassium bromide (KBr, 98%), ethylene glycol ($\text{CH}_2\text{OHCH}_2\text{OH}$, 98%), acetic acid (CH_3COOH , 99%), hydrogen peroxide (H_2O_2 , 99%), rhodamine B (RhB, 95%), and absolute ethanol ($\text{C}_2\text{H}_5\text{OH}$, 98%) were purchased from Sinopharm Chemical Reagent Co., Ltd. All the aqueous solutions were prepared by using ultrapure water (Milli-Q Biocel, 18 M Ω).

2.2 Synthesis of Fe(II)/Fe(III) doped Bi/BiOBr hierarchical microspheres

The Fe(II)/Fe(III) doped Bi/BiOBr photocatalysts were prepared by a solvothermal method. Typically, 3 mmol $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and a given amount of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ were dissolved in 30 mL ethylene glycol containing 3 mL acetic acid under magnetic stirring for 30 min. 3 mmol of KBr was dissolved in 30 mL ethylene glycol, and the resultant solution was added fast to the above mentioned $\text{Bi}(\text{NO}_3)_3$ solution with vigorous stirring for 30 min. Next, the mixture was transferred to a 100 mL Teflon autoclave, followed by solvothermal treatment at 433 K for 12 h. After naturally cooling to room temperature, the obtained sample was separated by centrifugation and washed with absolute ethanol and deionized water several times. Finally, the samples were freeze-dried under vacuum. The resultant products were denoted as *x*-FBB, where *x* (0.05, 0.1, 0.2, 0.4) refers to the ratio of Fe to Bi. All the operations were done under Ar atmosphere.

2.3 H_2O_2 -enhanced photocatalytic tests

The visible light-Fenton-like catalytic activities of Fe(II)/Fe(III) doped Bi/BiOBr were evaluated by the catalytic degradation of rhodamine B (RhB) solution with 5 mM H_2O_2 under visible light irradiation ($\lambda = 420$ nm). A 300 W Xe lamp with a 420 nm cut-off filter was used as a visible light source, and the vertical distance between the lamp and the liquid level was 15 cm. In every experiment, 50 mg of photocatalyst was added to 100 mL of 20 mg L⁻¹ RhB solution. Prior to illumination, the suspension was magnetically stirred in the dark for 30 min to ensure the establishment of an adsorption–desorption equilibrium between the photocatalyst and RhB. Af-

ter the addition of 5 mM H_2O_2 , the photocatalytic test was conducted with 1 mL reacting solution sampled at the desired time and then centrifuged to remove the photocatalysts.

The photocatalytic tests were the same as the H_2O_2 -enhanced photocatalytic tests, including the Fenton-like reaction, except for the addition of 5 mM H_2O_2 . The concentration of RhB was determined from the absorbance at the wavelength of 554 nm by a UV-visible spectrophotometer (UV-2990, Shimadzu, Japan).

2.4 Fe(II) regeneration

The amounts of Fe(II) generated on 0.5 g L⁻¹ 0.2-FBB without 20 mg L⁻¹ RhB were measured by photocatalytic reaction, Fenton-like reaction, and H_2O_2 -enhanced photocatalytic reaction experiments. The analysis of Fe(II) was carried out using 1,10-phenanthroline^{19,20} as follows: 2 mL suspended solution drawn from the reactor was mixed uniformly with 2 mL 0.5% 1,10-phenanthroline solution and 2 mL NaAc–HAc solution and centrifuged to measure the Fe(II) concentration. The total iron concentration was determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES, Prodigy, Leeman Co.).

2.5 Characterization

The phase structures of the samples were analyzed using an X-ray diffractometer (X'Pert PRO MPD, PANalytical) with a 2 θ scope of 5–90° at 40 kV and 40 mA using Cu K α as the irradiation source ($\lambda = 1.5406$ Å). The morphologies of the samples were measured using a field emission scanning electron microscope (FESEM, scanning voltage 10 kV) (SU-8020, Hitachi Limited) equipped with an energy-dispersive X-ray spectrometer. X-ray photoelectron spectroscopy with Al-K X-ray irradiation (ESCALAB 250Xi, Thermo Fisher Scientific) was used to examine the surface properties of the photocatalysts. The UV-vis diffuse reflectance spectra (UV-vis DRS) of the samples were recorded on a UV-vis spectrometer (Shimadzu UV-3600) with an integrating sphere using BaSO₄ as the reference. The Brunauer–Emmett–Teller (BET) specific surface area was measured using a fully automatic analyzer (ASAP2020HD88, Micromeritics Instrument Corp).

3. Results and discussion

3.1 Crystalline phase and morphology

XRD patterns of the as-prepared BiOBr and Fe(II)/Fe(III) doped Bi/BiOBr samples with different Fe/Bi ratios are shown in Fig. 1. It can be seen that all the diffraction peaks of the BiOBr samples match well with the standard data of the tetragonal phase of BiOBr (JCPDS card no. 09-0393). However, Fe(II)/Fe(III) doped Bi/BiOBr samples can be indexed to the tetragonal phase of BiOBr (JCPDS card no. 09-0393) and the rhombohedral phase of Bi (JCPDS card no. 44-1246). The peak intensities of the Bi crystal phase in Fe(II)/Fe(III) doped Bi/BiOBr samples were increased with the increase of Fe content. This indicates that the addition of Fe²⁺ can enhance the

Fig. 1 XRD patterns of BiOBr and Fe(II)/Fe(III) doped Bi/BiOBr with different Fe/Bi molar ratios (inset: diffraction peak position of {110} in the range of 28–34°).

growth of Bi metal nanoparticles, where Fe^{2+} cannot reduce Bi^{3+} to Bi^0 but contributes to the transformation of amorphous to crystalline phase (Fig. S1†). Amorphous Bi metal nanoparticles could exist in the BiOBr sample.²¹ The diffraction position of the {110} plane is observed in the inset of Fig. 1. The peak position of Fe(II)/Fe(III) doped Bi/BiOBr samples shifts slightly towards a higher 2θ value with the increase of Fe/Bi ratio, and other peaks exhibit a similar behavior. This shows that the differences in the ionic radius result in the changes of the lattice parameters.²² The ionic radius of Fe^{2+} (0.075 nm) is smaller than that of Bi^{3+} (0.103 nm), and the doped Fe may be incorporated into the BiOBr matrix by substituting for Bi^{3+} lattice sites.

Fig. 2 FESEM images of photocatalysts: (a) BiOBr, (b) 0.05-FBB, (c) 0.1-FBB, (d) 0.2-FBB, (e) 0.4-FBB; SEM (f), EDS (g), and mapping (h) of 0.2-FBB.

The microstructures, morphologies and particle sizes of the as-prepared BiOBr and Fe-doped BiOBr samples with different Fe/Bi ratios were investigated by FESEM. Fig. 2 and Fig. S2† show the SEM images and magnified images of the products, respectively. The image in Fig. 2a exhibits that the exterior surfaces of a BiOBr microsphere with a diameter of 8 μm were composed of many wheat-like nanoparticles. Fig. 2b–d displays that Fe(II)/Fe(III) doped Bi/BiOBr microspheres with diameters in the range of 3 to 5 μm in were formed of many nanosheets packed together. Fig. 2e shows that parts of the Fe(II)/Fe(III) doped Bi/BiOBr microspheres were inhibited. Chemical element mapping analysis (Fig. 2f–h) reveals that elements including Bi, O, Br, and Fe are uniformly distributed over the 0.2-FBB. Fig. S2† shows that BiOBr consisted of plenty of microspheres with diameters ranging from 6 to 10 μm while 0.05-FBB was composed of many microspheres with the range of diameters from 3 to 6 μm . This indicates that the addition of Fe ions can partly decrease the particle size of microspheres and enhance the growth of nanosheets.

The specific surface area and porosity of BiOBr and Fe(II)/Fe(III) doped Bi/BiOBr were measured by N_2 adsorption-desorption analysis, as shown in Fig. 3a. The isotherms belong to type IV with a distinct hysteresis loop observed in the

Fig. 3 N_2 adsorption-desorption isotherms (a) and pore size distribution (b) of BiOBr and Fe(II)/Fe(III) doped Bi/BiOBr samples.

range of 0.5–1.0 p/p_0 , which is characteristic of mesoporous materials. According to IUPAC recommendations,²³ the above hysteresis loops can be categorized as type H3 loops, which are reported for materials composed of aggregates (loose assemblages) of platelike particles forming slitlike pores. The BET specific areas of the products were calculated from N_2 adsorption–desorption isotherms. The products contained small mesopores (3.6 nm) and large mesopores with maximum pore diameters of *ca.* 15 nm, determined by using the Brunauer–Emmett–Teller (BET) method, as shown in Fig. 3b. The pore sizes, pore volumes and surface areas of the products increased with the increase of the Fe/Bi ratio, which is listed in Table 1. These results may be attributed to the inter-nanosheet spaces.

3.2 UV-vis DRS analysis

The optical properties of the as-prepared products were measured by a UV-vis spectrometer. Fig. 4 shows the UV-vis DRS spectra of BiOBr and Fe(II)/Fe(III) doped Bi/BiOBr samples. A steep increase of the absorption at wavelengths shorter than 450 nm can be assigned to the intrinsic band gap absorption of pure BiOBr (2.54 eV). UV-vis DRS of Fe(II)/Fe(III) doped Bi/BiOBr samples exhibit a systematic red shift and increased photoabsorption in the visible light range and near infrared region. This can also be concluded from a simple visual inspection of the samples since their colors gradually turn from white to reddish yellow. The enhanced photoabsorption in the visible light range can be attributed to the presence of oxygen vacancies and Bi metal.

3.3 Surface composition

The chemical compositions of BiOBr and Fe(II)/Fe(III) doped Bi/BiOBr samples were checked by XPS. As shown in Fig. 5a, the XPS survey spectrum reveals that Fe(II)/Fe(III) doped Bi/BiOBr samples are composed of Bi, O, Br, Fe and a trace amount of C, whereas BiOBr is composed of Bi, O, and Br, the peak positions of which are listed in Table S1.† Fig. 5b shows the XPS spectrum of Fe 2p in Fe(II)/Fe(III) doped Bi/BiOBr samples. The peaks at binding energies around 710 eV and 724 eV can be ascribed to Fe 2p_{3/2} and Fe 2p_{1/2}, respectively. The peak at 710 eV can be fitted into two peaks that are assigned to Fe²⁺ (709.6–709.9 eV) and Fe³⁺ (711.3–711.5 eV).²⁴ Fig. 5c exhibits the XPS spectrum of Bi 4f in BiOBr. The peaks at binding energies around 159 eV and 164 eV cor-

Fig. 4 UV-vis diffuse reflectance spectra of BiOBr and Fe(II)/Fe(III) doped Bi/BiOBr samples.

respond to Bi 4f_{7/2} and Bi 4f_{5/2}, respectively. The peak at 159 eV can be fitted into two peaks at 157.3 eV and 158.8 eV. The peak at 157.3 eV is assigned to Bi⁰ in Bi metal nanoparticles,^{13,25} whereas the peak at 158.8 eV is assigned to Bi³⁺ in BiOBr. The peaks of the Bi 4f_{7/2} XPS spectrum (Fig. 5d) for the 0.2-FBB sample can be deconvoluted to two individual peaks that are assigned to Bi⁰ (157.1 eV) and Bi³⁺ (158.3 eV). In addition, the peaks of the Bi 4f_{7/2} XPS spectra (Fig. S3†) for other Fe(II)/Fe(III) doped BiOBr samples can be fitted to two peaks at around 157.1 eV and 158.4 eV that correspond to Bi⁰ and Bi³⁺, respectively. This may be because the addition of ethylene glycol and CH₃COOH could enhance the rate of reduction of Bi³⁺ to Bi⁰ rather than Fe²⁺ reducibility.²¹ First, ethylene glycol has a more negative redox potential compared with the redox potential (0.308 eV) of Bi³⁺/Bi⁰;²⁶ second, the redox potential (0.77 eV) of Fe³⁺/Fe²⁺ is much higher than that of Bi³⁺/Bi⁰.²⁷

Fig. 5e displays that the peaks of O 1s in the XPS spectra in samples can be resolved into three peaks. The peaks at 529.5 eV, 530.8 eV, and 532.1 eV for BiOBr are attributed to Bi–O bonds in BiOBr, hydroxyl groups on the surface and oxygen deficient regions, respectively.^{26,27} The peaks shifted to low binding energy with the increase of the Fe/Bi molar ratio. This could be due to the substitution of the bismuth atom by the iron atom in the lattice and the hydroxy iron on the surface. The XPS spectra of Br 3d in the samples are shown in Fig. 5f. The peaks can be fitted into two peaks that correspond to Br 3d_{5/2} (67.4–67.9 eV) and Br 3d_{3/2} (68.4–68.9 eV), which are characteristic peaks of Br in BiOBr.

According to the atomic content of each element in samples in Table 1, we calculated the actual composition ratio of Fe(II) to Fe(III) in Fe(II)/Fe(III) doped Bi/BiOBr samples from peak areas. The Fe(II)/Fe(III) molar ratios of Fe(II)/Fe(III) doped Bi/BiOBr samples are 1.04–1.21, and the Fe/Bi molar ratios are 0.21–0.68, most of which are higher than the theoretical values. This probably results from iron oxides on the surface of samples, even inhibiting the photocatalytic activities of samples.

Table 1 Physical parameters of products obtained from N_2 isotherms and XPS

Samples	Surface area (m ² g ^{−1})	Pore size (nm)	Pore volume (cm ³ g ^{−1})	Fe(II)/Fe(III)	Surface Fe/Bi molar ratio
BiOBr	16.15	7.62	0.031	—	0
0.05-FBB	14.26	8.53	0.030	1.09	0.21
0.1-FBB	19.55	9.07	0.044	1.05	0.36
0.2-FBB	47.01	9.57	0.11	1.04	0.68
0.4-FBB	45.01	11.55	0.13	1.21	0.31

Fig. 5 XPS survey spectrum (a) of BiOBr and Fe(II)/Fe(III) doped BiOBr samples; high-resolution XPS spectra of Fe 2p (b), Bi 4f (c and d), O 1s (e), and Br 3d (f) in BiOBr and Fe(II)/Fe(III) doped BiOBr samples.

Fig. 6 The change of RhB concentration (C/C_0) (a) and pseudo-first-order reaction rate constants (b) of RhB degradation as a function of irradiation time by the as-prepared photocatalysts during the visible light-Fenton-like reaction ($[FBB] = 0.5 \text{ g L}^{-1}$; $[H_2O_2]_0 = 5 \text{ mM}$; $[RhB]_0 = 20 \text{ mg L}^{-1}$).

3.4 Visible light-Fenton-like catalytic activities

3.4.1 Catalytic activity of FBB. The visible light-Fenton-like catalytic activities of BiOBr and Fe(II)/Fe(III) doped Bi/BiOBr samples were evaluated *via* RhB degradation with an initial concentration of 20 mg L⁻¹. Fig. 6a shows changes in the concentration of RhB *versus* irradiation time during the visible light-Fenton-like catalytic degradation process. The blank test displays extremely low photodegradation on RhB, which could be almost ignored. After 30 min of adsorption-desorption equilibrium, 0.2-FBB shows the highest adsorption ability with 43% adsorption efficiency. After 60 min of illumination, the degradation efficiencies of RhB are 56.5%, 46.8%, 81.3%, 99.0%, and 95.2% for BiOBr, 0.05-FBB, 0.1-FBB, 0.2-FBB, and 0.4-FBB, respectively. The catalytic degradation process can be described by pseudo-first-order kinetics: $\ln(C/C_0) = -kt$, where k is the apparent rate constant as the basic kinetic parameter for different catalysts. Variations in $\ln(C_0/C)$ as a function of irradiation time are given in Fig. S4†. As seen from Fig. 6b, the kinetic rate constants of BiOBr, 0.05-FBB, 0.1-FBB, 0.2-FBB and 0.4 FBB are 0.0114 min⁻¹, 0.0092 min⁻¹, 0.0178 min⁻¹, 0.0449 min⁻¹, and 0.0326 min⁻¹, respectively. In view of the effects of surface areas on the RhB degradation, pseudo-first-order kinetics rate constant *versus* surface area is calculated (Fig. S5†). The results exhibit the higher catalytic activity per surface area for 0.1–0.2 Fe to Bi molar ratio in FBB. For FBB with the same surface area, the catalytic performance of 0.2-FBB is significantly higher than that of 0.4-FBB. This implies that the combination of surface area and higher catalytic active sites contributes to the highest catalytic activity for 0.2-FBB.

In the Fenton-like reaction and photocatalytic reaction, the kinetic rate constants of 0.05-FBB, 0.1-FBB, 0.2-FBB and 0.4 FBB are 0.00165 min⁻¹, 0.00263 min⁻¹, 0.00445 min⁻¹, 0.00172 min⁻¹ and 0.00168 min⁻¹, 0.00179 min⁻¹, 0.00269 min⁻¹, 0.0003 min⁻¹, respectively, which are far less than those in the visible light-Fenton-like reaction. This suggests that H₂O₂ can activate the catalytic active sites of Fe(II)/Fe(III) doped Bi/BiOBr under visible light.

3.4.2 Comparisons of Fe(II)/BiOBr, Fe(III)/BiOBr and 0.2-FBB. The external supply of Fe(II) or Fe(III) ions to the BiOBr system (Fe(II)/BiOBr or Fe(III)/BiOBr) was studied in the photo-Fenton-like catalytic reaction. The result shows that the two reaction systems inhibit RhB degradation (Fig. 7). For example, the RhB degradation efficiencies in the Fe(II)/BiOBr, Fe(III)/BiOBr, BiOBr, and 0.2-FBB systems are 45.2%, 52.0%, 57.7% and 95.1% within 60 min, respectively, and the reaction rate constants are 0.0077 min⁻¹, 0.0101 min⁻¹, 0.0114 min⁻¹, and 0.045 min⁻¹, respectively. Compared with the 0.2-FBB system, the simple mixing system (Fe(II)/BiOBr or Fe(III)/BiOBr) shows the lowest RhB degradation rate. This implies that RhB in the physical mixing systems cannot be removed well by capturing photoelectrons and the Fenton-like reaction.

3.5 Stability of catalysts

The catalytic stability of 0.2-FBB was investigated *via* a cycling experiment. After the RhB adsorption equilibrium was completed, the reaction system was centrifuged to regenerate the photocatalysts for RhB degradation in the visible-light-Fenton-like reaction. Fig. 8 compares the degradation degrees of RhB in the different cycling experiments, and the results reveal that the degradation efficiency of RhB slightly decreases after 5 cycles. This implies that 0.2-FBB exhibits excellent visible-light Fenton-like catalytic stability.

3.6 Visible light Fenton-like catalytic reaction mechanism

3.6.1 Active species. Usually, a large surface area can provide more adsorption sites, and even more catalytic sites. As shown in Table 1, 0.2-FBB has the largest BET surface area with a higher adsorption amount and shows higher catalytic efficiency during the visible light-Fenton-like reaction. We carried out radical trap tests to investigate the active species of 0.2-FBB during the visible light-Fenton-like catalytic process. The degradation of RhB was repeated with 5 mM H₂O₂ under visible light irradiation by adding 1 mM ascorbic acid (AA) as a superoxide radical ([•]O₂⁻) scavenger,^{28,29} 10 mM of isopropanol (IPA) as a hydroxyl radical scavenger ([•]OH)^{30,31}

Fig. 7 RhB degradation under different systems ($[BiOBr \text{ or } 0.2-FBB] = 0.5 \text{ g L}^{-1}$; $[H_2O_2]_0 = 5 \text{ mM}$; $[RhB]_0 = 20 \text{ mg L}^{-1}$; $[Fe(II)/Fe(III)]_0 = 18 \text{ mg L}^{-1}$).

Fig. 8 Five cycles on the degradation of RhB by 0.2-FBB under visible light and H_2O_2 after adsorption equilibrium ($[\text{0.2-FBB}] = 0.5 \text{ g L}^{-1}$; $[\text{RhB}]_0 = 10 \text{ mg L}^{-1}$; $[\text{H}_2\text{O}_2]_0 = 5 \text{ mM}$).

Fig. 10 The change of surface Fe(II) concentration on the 0.2-FBB with or without H_2O_2 under visible light ($[\text{0.2-FBB}] = 0.5 \text{ g L}^{-1}$; $[\text{H}_2\text{O}_2]_0 = 5 \text{ mM}$).

and 10 mM of triethanolamine (TEOA) as a h^+ scavenger.³² Fig. 9a displays the effect of scavengers on the RhB degradation. The RhB degradation efficiency is completely inhibited by TEOA, while there is only weak inhibition on the RhB degradation with the addition of IPA. The presence of AA can slightly increase the degradation of RhB. The change in $\ln(C_0/C)$ as a function of irradiation time is presented in Fig. 9b. The pseudo-first-order reaction constants of RhB with no scavenger and with IPA, TEOA and AA are 0.048 min^{-1} , 0.031 min^{-1} , 0.00026 min^{-1} , and 0.051 min^{-1} , respectively (Fig. 9c). This indicates that the effect of active species on

RhB degradation by 0.2-FBB follows the order holes > hydroxyl radicals > superoxide radicals.

In Fig. 9d, the addition of AA can increase the amount of released Fe from 0.2-FBB into solution while there was almost no Fe released from 0.2-FBB for other tests without AA, indicating the formation of a Fe-AA complex. The redox reaction of Fe(III) to Fe(II) is decreased by the Fe-AA complex to catch more photogenerated electrons under visible light,^{33,34} producing more holes to degrade RhB. In Fig. S6,[†] AA can still increase the RhB degradation efficiency in the absence

Fig. 9 Effect of different scavengers on the RhB degradation by 0.2-FBB under visible light and 5 mM H_2O_2 : (a) RhB degradation efficiency, (b) change in $\ln(C_0/C)$ as a function of irradiation time, (c) pseudo-first-order reaction rate constants (k), and (d) released Fe concentration ($[\text{0.2-FBB}] = 0.5 \text{ g L}^{-1}$; $[\text{H}_2\text{O}_2]_0 = 5 \text{ mM}$; $[\text{TEOA}]_0 = 10 \text{ mM}$; $[\text{IPA}]_0 = 10 \text{ mM}$; $[\text{AA}]_0 = 1 \text{ mM}$).

Fig. 11 H_2O_2 decomposition under different systems: (a) photo-Fenton-like reaction on 0.2-FBB; (b) Fenton-like reaction on 0.2-FBB; and (c) photo-Fenton-like reaction on BiOBr ($[\text{0.2-FBB}]$ or $[\text{BiOBr}] = 0.5 \text{ g L}^{-1}$; $[\text{H}_2\text{O}_2]_0 = 10 \text{ mM}$).

of H_2O_2 under visible light. Therefore, both H_2O_2 and AA can improve the catalytic activity of 0.2-FBB under visible light.

3.6.2 Surface Fe(II) generation and H_2O_2 decomposition. To further investigate how H_2O_2 can activate the photocatalytic active sites, surface Fe(II) concentration over 0.2-FBB under different systems was measured. Fig. 10 shows that it is increased and then quickly decreased in the visible light-Fenton-like reaction, while the Fe(II) concentration was decreased in the Fenton-like reaction (Fig. 10). In contrast, the change trend of Fe(II) concentration in the photocatalytic reaction is almost the same as that in the visible light-Fenton-like reaction. This suggests that Fe(III) is reduced to Fe(II) by the photoelectrons produced by 0.2-FBB under visible light (eqn (4) and (5)),^{35–37} while the presence of H_2O_2 can increase the oxidation rate of Fe(II) to Fe(III), reducing the surface Fe(II) concentration over 0.2-FBB.

Fig. 13 The scheme of visible light-Fenton-like catalytic reaction mechanism.

Fig. 11 displays the H_2O_2 decomposition at different reaction systems. The decomposition rate constants of the photo-Fenton-like reaction (0.2-FBB), Fenton-like reaction (0.2-FBB) and photo-Fenton-like reaction (BiOBr) were 0.033 min^{-1} , 0.00065 min^{-1} and 0.0033 min^{-1} , respectively. In the photo-Fenton-like reaction by BiOBr, H_2O_2 acts as an electron capture agent (eqn (6)), where its rate constant is far less than that in the photo-Fenton-like reaction of 0.2-FBB. This indicates that H_2O_2 not only joins in capturing the photoelectrons, but also plays an important role in the other reactions.³⁵ After catalytic reaction within 120 min, the final pH of the Fenton-like reaction (0.2-FBB), photo-Fenton-like reaction (0.2-FBB), and photo-Fenton-like reaction (BiOBr) is 4.09, 4.31 and 4.59. In the Fenton-like reaction, pH is decreased by Fe(III) reacting with H_2O_2 (eqn (2)), which indicates that large amounts of H_2O_2 participate in the Fenton-like reaction for 0.2-FBB under visible light.

3.6.3 ESR spectroscopy. The EPR technique with DMPO as a spin-trapping agent was used to further identify the production of $\cdot\text{OH}$ in the BiOBr/ H_2O_2 and 0.2-FBB/ H_2O_2 systems under visible light (Fig. 12). The BiOBr/ H_2O_2 and 0.2-FBB/ H_2O_2 systems show the signal of the DMPO- $\cdot\text{OH}$ spin adduct, 1 : 2 : 2 : 1 quartet lines with hyperfine constants $a_N = a_H = 14.96 \text{ G}$.³⁸ A notable observation is that the signal intensity of the 0.2-FBB/ H_2O_2 system is much higher than that of the BiOBr/

Fig. 12 EPR spectra obtained by spin trapping with DMPO in photo-Fenton-like reactions ($[\text{BiOBr}]$ or $[\text{0.2-FBB}] = 0.5 \text{ g L}^{-1}$; $[\text{H}_2\text{O}_2]_0 = 10 \text{ mM}$; $[\text{DMPO}]_0 = 10 \text{ mM}$).

H₂O₂ system, which confirms the production of more hydroxyl radicals by 0.2-FBB in the photo-Fenton-like reaction.

Based on the above discussion, we propose the H₂O₂-enhanced photocatalytic reaction mechanism of RhB degradation by 0.2-FBB (Fig. 13) as follows: (1) reduction of Fe(III) to Fe(II) by photoelectrons obtained from 0.2-FBB under visible light; (2) Fe(II) reaction with H₂O₂ producing more hydroxyl radicals; (3) more holes remain after photoelectron capture, where holes and hydroxyl radicals are used to rapidly degrade the organic molecules.

4. Conclusions

In summary, Fe(II)/Fe(III) doped Bi/BiOBr (FBB) hierarchical microspheres with heterojunctions as novel visible light photocatalysts were successfully obtained by a simple solvothermal method. It has been demonstrated that the addition of Fe can play an important role in the growth of the Bi metal crystal phase and increase the BET specific surface areas of Fe(II)/Fe(III) doped Bi/BiOBr samples. 0.2-FBB displayed the highest catalytic performance for RhB degradation in the visible light-Fenton-like reaction. This is attributed to the increasing reduction rate of $\equiv\text{Fe(III)}$ to $\equiv\text{Fe(II)}$ by photoelectrons, producing more holes and hydroxyl radicals to degrade RhB, which is verified by the ESR technique and H₂O₂ consumption and surface Fe(II) measurement experiments. The radical scavenger experiments suggest that holes play a key role in the RhB degradation. In addition, 0.2-FBB is quite stable in the catalytic performance.

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