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Article

2D/2D step-scheme α -Fe₂O₃/Bi₂WO₆ photocatalyst with efficient charge transfer for enhanced photo-Fenton catalytic activity

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ABSTRACT

Although the traditional Fenton reaction is considered an effective strategy for solving problems caused by environmental pollution, construction of an efficient photocatalytic system by coordinating the Fenton reaction is challenging. In this study, 2D/2D step-scheme α -Fe₂O₃/Bi₂WO₆ (FO/BWO) heterostructure photo-Fenton catalysts were successfully fabricated by a facile hydrothermal method. The as-prepared materials were characterized by XRD, FT-IR, TEM, XPS, UV-vis DRS, PL, I-t, EIS, and BET analyses. Under visible light irradiation, FO/BWO exhibited remarkably high and stable photo-Fenton catalytic activity for the degradation of methyl blue (MB) at low concentrations of H₂O₂. It was noted that FO/BWO (0.5) displayed a significantly enhanced photo-Fenton catalytic activity, which was 11.06 and 3.29 times those of FO nanosheets and BWO nanosheets, respectively. The notably improved photo-Fenton catalytic activity of FO/BWO was mainly due to the combination of H₂O₂ and FO under light illumination and the presence of the 2D/2D S-scheme heterostructure, with the large contact surface, abundant active sites, and efficient separation rate of photogenerated carriers playing contributory roles. Additionally, a possible catalytic mechanism for the FO/BWO composite was preliminarily proposed via active species trapping experiments. In summary, this study provided new insights into the synthesis of an effectively heterogeneous 2D/2D S-scheme photo-Fenton catalyst for degradation of organic pollutants in wastewater.

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1. Introduction

Since the discovery of the Fenton reaction in 1894, it has been considerably explored and widely applied, especially when it came to the decomposition of organic pollutants in water [1,2]. As an important advanced oxidation process (AOP), the traditional homogeneous Fenton reaction could generate strongly oxidizing hydroxyl radicals ($\cdot$ OH) by activating H₂O₂ with Fe²⁺, which could be used for the treatment of refractory organics. The Fenton reaction possesses advantages of low

toxicity, fast reaction speed, and simple operation. It can degrade wastewater during the process of wastewater treatment, and, together with other after-treatment processes, allow for the reuse of water [3]. However, following main shortcomings were observed for the Fenton reaction: (1) a large quantity of acids were needed to maintain the acidic environment during the Fenton reaction to ensure the optimum activity of the reaction; (2) iron ions were constantly lost; and (3) solid sludges, which seriously polluted the environment, were formed in the Fenton reaction [4]. Therefore, it was of great significance to

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develop an efficient photo-Fenton catalyst with the advantages of expanding the effective range of acidity and multiple recoverability.

The synergistic effect of photocatalysis and the Fenton reaction could promote the charge transfer between Fe^{3+} and Fe^{2+} by utilizing photogenerated carriers and improve the degradation rate of organic pollutants [5–13]. Recently, iron-based photocatalysts, especially $\alpha\text{-Fe}_2\text{O}_3$, have been extensively studied in the field of heterogeneous photo-Fenton catalysis. On the one hand, as a photo-Fenton catalyst, $\alpha\text{-Fe}_2\text{O}_3$ could initiate the photo-Fenton reaction under almost neutral conditions, eliminating the need to adjust the pH value at all times in the reaction process. On the other hand, Fe^{3+} could be reduced to Fe^{2+} by the electrons on the conduction band (CB) of $\alpha\text{-Fe}_2\text{O}_3$, which reduces the loss of Fe^{2+} and the production of solid sludge [14–16]. Nevertheless, a single $\alpha\text{-Fe}_2\text{O}_3$ photocatalyst still exhibit poor photocatalytic activity due to the migration kinetics and sluggish separation of photogenerated carriers [17–20]. The previous studies found that the construction of the heterojunction was an efficient method for improving the photocatalytic activity of catalyst [21–41]. In particular, the 2D/2D heterostructure composite with intimate face-to-face contact possessed a larger interfacial region between 2D $\alpha\text{-Fe}_2\text{O}_3$ and another 2D photocatalyst, which reduced the charge transport time and distance between the 2D nanosheets and increased the specific surface area of the materials [42–45]. In addition, the S-scheme-system (S-scheme) heterojunction that was proposed by Yu *et al.* [46–50] to improve the charge-separation efficiency and redox ability of photocatalysts could overcome the defects of the type-II heterojunction. Under the driving force of an interfacial built-in electric field, the e^- in the CB of the oxidation photocatalyst recombined with the h^+ in the valence band (VB) of the reduction photocatalyst, which could spatially separate the h^+ in the VB of the oxidation photocatalyst and the e^- in the CB of the reduction photocatalyst and retain the strong oxidizing ability and reducing capacity of the catalyst. Therefore, the photocatalytic activity of $\alpha\text{-Fe}_2\text{O}_3$ might be improved by constructing a 2D/2D S-scheme-systems heterojunction.

Recently, Bi_2WO_6 , as a visible-light-driven photocatalyst, has been widely studied owing to its unique layered structure and stable chemical properties [51–56]. Suitable band gap matching was reported to exist between $\alpha\text{-Fe}_2\text{O}_3$ and Bi_2WO_6 that facilitated the formation of a heterojunction photocatalytic system [57–62]. For instance, the degradation rate of gas-phase benzene over the $\alpha\text{-Fe}_2\text{O}_3/\text{Bi}_2\text{WO}_6$ composite synthesized via the hydrothermal method was about 2.5 times higher than that of Bi_2WO_6 [63]. Owing to the construction of the heterogeneous interface between Bi_2WO_6 and $\alpha\text{-Fe}_2\text{O}_3$, the photocatalytic activity toward the degradation of organic contaminants under visible light irradiation of the $\alpha\text{-Fe}_2\text{O}_3/\text{Bi}_2\text{WO}_6$ composite with a sphere-like hierarchical structure was significantly improved [64]. However, to the best of our knowledge, there are few studies on 2D/2D S-scheme-system $\alpha\text{-Fe}_2\text{O}_3/\text{Bi}_2\text{WO}_6$ heterojunctions combined with the heterogeneous Fenton reaction. Herein, it could be expected that the synergetic reaction of the 2D/2D S-scheme $\alpha\text{-Fe}_2\text{O}_3/\text{Bi}_2\text{WO}_6$ composite and the hetero-

geneous Fenton reaction could improve the degradation rate of organic pollutants.

In this study, a 2D/2D S-scheme $\alpha\text{-Fe}_2\text{O}_3/\text{Bi}_2\text{WO}_6$ heterostructure photo-Fenton catalyst was designed and prepared by a facile hydrothermal method. The crystal structure, elemental states, microstructural morphology, optical properties, and chemical composition of the catalysts were characterized. The photo-Fenton catalytic activities of these composites were evaluated by the degradation of MB in the presence of H_2O_2 under visible light irradiation. The result of the degradation experiments indicated that the $\alpha\text{-Fe}_2\text{O}_3/\text{Bi}_2\text{WO}_6$ composite combined with a heterogeneous Fenton reaction displayed superior photo-Fenton catalytic activity compared to $\alpha\text{-Fe}_2\text{O}_3$ and Bi_2WO_6 catalysts. Furthermore, to explore the heterogeneous Fenton reaction and the photocatalytic process, the degradation kinetics, catalytic mechanism, and stability test of the catalysts were determined. In this study, $\alpha\text{-Fe}_2\text{O}_3$ and Bi_2WO_6 nanosheets were successfully combined to effectively degrade the organic pollutants under visible light, which sufficiently met the urgent requirements of environmental protection.

2. Experimental

2.1. Materials

The materials included sodium tungstate dihydrate ($\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$), bismuth nitrate pentahydrate ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$), cetyltrimethylammonium bromide (CTAB), ferric nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), sodium acetate (CH_3COONa), absolute ethanol, H_2O_2 , and deionized water. All chemical reagents were of analytical grade and were used as received without further purification.

2.2. Preparation of $\alpha\text{-Fe}_2\text{O}_3/\text{Bi}_2\text{WO}_6$

2.2.1. Synthesis of Bi_2WO_6

The preparations of 2D ultrathin Bi_2WO_6 nanosheets were based on the micro-modification methods reported in the literature [65]. Essentially, 1 mmol of $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ and 0.05 g of CTAB were successively dissolved in 70 mL of deionized water by sonication. Subsequently, 2 mmol of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ powder was added to the above solution with vigorous stirring until a homogeneous suspension was formed. Finally, the mixture was transferred to a 100 mL Teflon-lined stainless-steel autoclave and followed by hydrothermal treatment at 120 °C for 24 h. After natural cooling to room temperature, the products were collected via centrifugation and rinsed three times with absolute ethanol and deionized water. Subsequently, the obtained samples were dried at 60 °C overnight.

2.2.2. Synthesis of the $\alpha\text{-Fe}_2\text{O}_3/\text{Bi}_2\text{WO}_6$ composite

First, 0.0087 g of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was added to 60 mL of absolute ethanol followed by 3.5 mL of deionized water under magnetic stirring for 30 min at room temperature. Then, 0.0171 g of sodium acetate and 0.3 g Bi_2WO_6 were vigorously stirred for 30 min to acquire a uniform suspension. The weight ratio of $\alpha\text{-Fe}_2\text{O}_3$ to Bi_2WO_6 was 0.5:100. Afterwards, the mixed

solution was transferred to a 100 mL Teflon-lined stainless-steel autoclave and maintained at 180 °C for 24 h. The reactor was then allowed to cool to room temperature naturally. Finally, the resultant product was collected, washed with absolute ethanol and deionized water three times, and dried at 60 °C overnight. Herein, α -Fe₂O₃/Bi₂WO₆ with 0.3, 0.5, and 1 wt% mass ratios of α -Fe₂O₃ were noted as FO/BWO (0.3), FO/BWO (0.5), and FO/BWO (1), respectively.

2.3. Characterization

The phase structures of α -Fe₂O₃, Bi₂WO₆, and α -Fe₂O₃/Bi₂WO₆ nanocomposites were studied by X-ray powder diffraction (XRD) patterns on a DX2700 diffractometer (Haoyuan Instrument, China) under Cu K α radiation in a 2 θ range of 10°–80°. Diffuse reflectance spectroscopy (DRS) was recorded by a UV-2600 spectrophotometer (Shimadzu, Japan) in the range of 250–800 nm. A Fourier transform infrared (FT-IR) spectrum was obtained by a Nicolet iS5 spectrometer (Thermo Fisher Scientific, USA) with a frequency range from 3500 to 400 cm⁻¹. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images of the samples were recorded by FEI Tecnai G2 F20 for investigating the morphologies of α -Fe₂O₃, Bi₂WO₆, and α -Fe₂O₃/Bi₂WO₆ nanocomposites. X-ray photoelectron spectroscopy (XPS) was recorded by ESCALAB 250xi (Thermo, USA) for determining the surface elemental composition. The Brunauer Emmett Teller (BET) surface areas of the samples were obtained by an analyzer (Quadrascorb-evo, Quantachrome, USA) at 77 K. A FLSP920 fluorescence spectrophotometer (Edinburgh instruments, UK) was employed to investigate the PL spectra of α -Fe₂O₃, Bi₂WO₆, and α -Fe₂O₃/Bi₂WO₆ nanocomposites at the excitation wavelength of 327 nm. Using the Pt plate as the counter electrode and Ag/AgCl electrode as the reference electrode, an electrochemical analysis was carried out in a traditional three-electrode cell.

2.4. Photo-Fenton catalytic activity

The photo-Fenton catalytic activities of FO/BWO catalysts were investigated by using a 300 W xenon lamp with a cutoff filter ($\lambda \geq 400$ nm) to decompose MB (5 mg/L). The photocatalytic reaction was processed in a 150 mL Pyrex glass vessel. Typically, catalysts (20 mg) were added to 100 mL of the aqueous solution of MB in the reactor with vigorous magnetic stirring for an hour in the dark to achieve desorption-adsorption equilibrium of reagents. The initial pH value of the solution was 7, and the stirring rate was 600 rpm. A total of 100 μ L of hydrogen peroxide (H₂O₂, 30 wt%) was added to the reactor while the reagents were exposed to the xenon lamp. A total of 3 mL of the reaction liquid was collected every 5 min during the irradiation and centrifuged at 6000 rpm for 15 min. The collected solution was analyzed by UV-vis spectrometer (Shimadzu, Japan). The MB solution with a degradation rate of 100% was placed in the oven for drying. Residual catalysts were collected. Similar to the photocatalytic activity tests of the as-prepared photocatalysts, the collected catalysts were used

for photocatalytic degradation of MB. This procedure was repeated four times to test the stability of the catalyst.

3. Results and discussion

3.1. Characterizations of catalysts

Fig. 1 shows the XRD of the BWO, FO, and FO/BWO (x) (x = 0.3, 0.5, 1) samples. Four characteristic peaks can be seen for BWO at 28.3°, 32.3°, 47.1°, and 55.8°, indexing as the (113), (200), (202), and (311) crystallographic planes of orthorhombic BWO, respectively [66]. The diffraction peaks at the 2 θ values of 24.1°, 33.2°, 35.6°, 40.9°, 49.5°, 54.1°, 57.6°, 62.4°, and 64.0° corresponded to the (012), (104), (110), (113), (024), (116), (018), (214), and (300) planes of FO, respectively. It was notable that due to the low crystallinity and low content of FO, no typical diffraction peak of FO was found in the FO/BWO samples. The results indicated that FO with a low mass ratio had a negligible effect on the crystal surface of the BWO nanosheets. Moreover, no additional impurity diffraction peak was observed in all the samples, which indicated their high purity.

TEM and HRTEM were performed to investigate the microstructures and morphologies of FO, BWO, and the FO/BWO composites. As shown in Figs. 2(a) and 2(b), the FO samples displayed a uniform hexagonal nanoplate structure. In contrast, Figs. 2(c) and 2(d) show the aggregation morphologies of irregular BWO nanosheets with a size of tens of nanometers. It can be clearly seen that the FO nanosheets were deposited on the surface of BWO nanosheets, forming a 2D/2D structure (Fig. 2(e)). In the HRTEM image (Fig. 2(f)), lattice fringes with a fringe spacing of 0.315 and 0.221 nm could be observed. The two types of lattice fringes matched the (131) plane of BWO and the (113) plane of FO [53,67]. Therefore, the formation of the 2D/2D FO/BWO heterojunction was confirmed by HRTEM. In addition, the specific surface areas of FO, BWO, and FO/BWO (0.5) were studied by BET analysis. The experimental data revealed that the specific surface area of FO/BWO (0.5) (27.44 m²/g) was higher than those of FO (19.31 m²/g) and BWO (16.00 m²/g). The results indicated that the specific surface area of FO/BWO (0.5) increased due to the construction of the

Fig. 1. X-ray diffraction patterns of BWO, FO, FO/BWO (1), FO/BWO (0.5) and FO/BWO (0.3) photocatalysts.

Fig. 2. TEM images of (a-b) FO, (c-d) BWO, (e) FO/BWO (0.5) composite and (f) HRTEM image of FO/BWO (0.5) composite.

2D/2D heterojunction, which was helpful in improving the photo-Fenton catalytic activity.

XPS characterization (Fig. 3) was performed to identify the surface chemical compositions and chemical states of FO, BWO,

and FO/BWO (0.5). As shown in Fig. 3(a), the survey scan XPS spectra of FO/BWO (0.5) showed the presence of W, Bi, C, O and Fe. In Fig. 3(b), the peaks with binding energies of 529.8 and 532.1 eV were assigned to surface lattice oxygen and adsorbed oxygen, respectively. The two characteristic peaks of W 4f shown in Fig. 3(c) with binding energies of 36.7 and 34.6 eV respectively corresponded to the W 4f_{7/2} and W 4f_{5/2} of the W⁶⁺ ions. Fig. 3(d) shows that there are two separate peaks in the Bi 4f region of 163.9 eV and 158.5 eV, which corresponded to Bi 4f_{7/2} and Bi 4f_{5/2}, respectively. Compared with that of BWO, the binding energies of FO/BWO (0.5) on Bi 4f and W 4f increased significantly. As shown in Fig. 3(e), the Fe 2p peaks, which were ascribed to Fe 2p_{3/2} and Fe 2p_{1/2}, could be fitted onto peaks at 712.3 and 726.1 eV, respectively [68]. Overall, the W 4f, Bi 4f, O 1s, and Fe 2p elements of FO/BWO (0.5) displayed obvious movement compared with those of FO and BWO, which indicated that FO and BWO had a strong chemical interaction in FO/BWO (0.5).

The optical absorption spectra of the samples were analyzed by the UV-vis DRS technique. Figure 4 shows that the photo-absorption of BWO was ~420 nm, which is in the range of visible light. Furthermore, FO exhibited an absorption edge of about 580 nm in the visible region [69]. The visible light absorption of FO was due to the direct transition of O²⁻ (2p) to Fe³⁺ (3d) and the indirect transition of Fe³⁺ (3d) electrons. Compared with pure BWO, the absorption edge of FO/BWO displayed a certain red shift, which could be attributed to the presence of FO in the composite, although no iron oxide was detected by XRD. In theory, this result indicated that the FO/BWO composite was more effective when sunlight was used as the energy source for degradation of pollutants.

The chemical interaction between FO and BWO in FO/BWO was characterized by FT-IR spectroscopy. As shown in Fig. 5(a), a series of characteristic absorption peaks located at 500–1000 cm⁻¹ belong to BWO, which represented the bridging stretching

Fig. 3. XPS spectra of BWO, FO and FO/BWO (0.5) samples: (a) survey, (b) O 1s, (c) W 4f, (d) Bi 4f and (e) Fe 2p.

Fig. 4. UV-vis spectra of BWO, FO, FO/BWO (0.5), FO/BWO (0.3) and FO/BWO (1) photocatalysts.

modes of Bi-O, W-O, and W-O-W in BWO [44,70]. The amplified FT-IR spectra of the samples are shown in Fig. 5(b). A series of peaks located at 418 and 456 cm^{-1} were due to Fe-O stretching and bending modes, respectively [71–72]. The main spectrum of BWO was found to exist in the spectra of the FO/BWO composite. The strong absorption peaks of FO and BWO shifted slightly, indicating that the electronic structures of FO and BWO interacted strongly.

3.2. Photo-Fenton catalytic activity

The photocatalytic activities of the as-prepared catalysts were evaluated by the degradation of MB under visible light irradiation. In the presence of 0.1 mL H_2O_2 , the photo-Fenton catalytic activities of BWO, FO, and FO/BWO for the degradation of MB molecules were obtained and are displayed in Fig. 6(a). After 25 min of the photo-Fenton reaction, the degradation rate of pure BWO nanosheets was about 77.5%. The pho-

Fig. 5. FT-IR spectra of BWO, FO, FO/BWO (1), FO/BWO (0.3) and FO/BWO (0.5) photocatalysts.

to-Fenton activities of FO/BWO composites significantly increased. The degradation rate of MB over FO/BWO (0.5) was close to 100% within 25 min. However, the degradation of MB over FO/BWO composites decreased gradually when the content of FO in the composites exceeded its optimal level (0.5 wt%). The result might be due to the excessive amount of FO nanosheets that covered the active sites of FO/BWO composites. As shown in Fig. 6(b) and 6(c), the apparent rate constants (k) of FO/BWO (0.5), FO/BWO (1), and FO/BWO (0.3) were 0.1895, 0.0889 and 0.065 min^{-1} , respectively. The results indicated that the photo-Fenton catalytic activities of FO/BWO photocatalysts with different proportions were higher than those of FO (0.0171 min^{-1}) and BWO (0.0574 min^{-1}). It was obvious that FO/BWO (0.5) displayed the optimum photo-Fenton catalytic activity. In addition, to determine the effects of visible light irradiation, H_2O_2 , and a catalyst on MB degradation, more photo-Fenton degradation procedures were implemented. As shown in Fig. 6(d), when only H_2O_2 was added to a catalyst-free reaction system, the dye molecules could hardly be decomposed, which indicated that pure H_2O_2 could not de-

Fig. 6. (a) Dynamic curves of photodegradation for MB solution over different samples, (b) kinetic fitting of the photodegradation for MB solution over different samples, (c) degradation rate of the MB solution after 25 min. (d) degradation of MB under different reaction conditions.

Fig. 7. (a) XRD patterns of FO/BWO (0.5) photocatalyst before and after photodegradation experiment. (b) The recyclability of FO/BWO (0.5) for photocatalytic degradation of MB.

compose the dye effectively. The photo-Fenton catalytic activity of the FO/BWO composite was still higher than those of FO and BWO without H_2O_2 addition, which was due to the influence of the FO/BWO heterojunction. In the dark, the FO/BWO composite could hardly degrade MB after five minutes in the presence of H_2O_2 . The degradation of MB in the first five minutes might be the effect of the Fenton reaction. Nevertheless, when visible light irradiated the reaction system, the degradation rate of MB over FO/BWO increased significantly, which indicated that the visible light played a leading role in promoting the degradation rate. The circulating experiments were conducted to test the reusability and stability of the catalysts. FO/BWO (0.5) with the optimum photo-Fenton catalytic activity was selected as the model photocatalyst. As shown in Fig. 7(b), the photo-Fenton catalytic activity exhibited no obvious change in the five times degradation experiments, which indicated that the composite had good stability. In addition, the XRD pattern of the FO/BWO (0.5) composite was not significantly different before and after the photodegradation reaction, which suggested that the crystal structure of the sample was maintained (Fig. 7(a)). The results indicated that the FO/BWO (0.5) photo-Fenton catalyst had good stability.

Fig. 8. Photoluminescence emission spectra for FO, BWO and FO/BWO (0.5) photocatalysts. The wavelength of excitation light for fluorescence emission spectra was 327 nm.

3.3. Photo-Fenton catalytic reaction mechanisms

The fluorescence emissions of semiconductor materials are the result of a recombination of photogenerated electrons and holes. Therefore, photoluminescence (PL) analysis is used to study the migration, transfer, and recombination of photogenerated carriers in samples. As shown in Fig. 8, the PL spectra of FO, BWO, and the FO/BWO (0.5) composite were measured at 327 nm. BWO displayed the strongest emission peak in the range of 340–470 nm, which indicated that the recombination rate of photogenerated electron hole pairs was a maximum in BWO. The results revealed that for the FO/BWO composite, the strength of the emission band was significantly reduced, which indicated that the introduction of FO on BWO could greatly inhibit the recombination of photogenerated electron hole pairs and improve the separation rate of photogenerated carriers. In addition, a large specific surface area and 2D/2D S-scheme heterostructure of the FO/BWO composite were also conducive to the photodegradation of pollutant molecules on the surface of the composite.

To study the photocurrent response of FO/BWO to visible light, transient photocurrent analysis of the FO/BWO heterojunction was carried out. As shown in Fig. 9, the FO/BWO (0.5) composite, the photocurrent responses of FO and BWO were

Fig. 9. Transient photocurrent responses for the FO, BWO and FO/BWO (0.5) composite.

tested under four on-off cycles of intermittent illumination. The results suggested that the photocurrent response of the FO/BWO (0.5) heterojunction was significantly higher than those of FO and BWO, which indicated higher ability of the composite to generate and transmit photogenerated carriers than that of pure FO and pure BWO. In addition, electrochemical impedance spectroscopy (EIS) was conducted to determine the electron-transfer rate of the catalysts. The EIS measurements of FO/BWO (0.5), FO, and BWO were carried out at an amplitude of 5 mV in the frequency range of 0.1–1000000 Hz. As displayed in Fig. 10, the EIS Nyquist plots of all the catalysts displayed similar semicircles at high frequencies, while a smaller arc radius generally indicated a smaller transfer resistance on the electrode interface. The arc radius of the FO/BWO (0.5) composite was smaller than that of FO and BWO, which indicated that FO/BWO (0.5) displayed lower transfer resistance of photogenerated carriers than FO and BWO because of the 2D/2D S-scheme heterojunction structure. All of these results indicated the occurrence of enhanced charge transfer in FO/BWO (0.5), which contributed to the improved photo-Fenton catalytic activity of FO/BWO.

By introducing isopropyl alcohol (IPA), ethylenediaminetetraacetic acid (EDTA), and benzoquinone (CP), the main active species in the catalytic process were determined. IPA, EDTA, and CP were effective $\cdot\text{OH}$, h^+ , and $\cdot\text{O}_2^-$ scavengers, respectively [71]. As displayed in Fig. 11, the degradation rate of MB was reduced with the addition of any scavenger, which meant that $\cdot\text{O}_2^-$, $\cdot\text{OH}$, and h^+ all participated in the photocatalytic oxidation process. In addition, the degradation rate of MB slightly decreased with the addition of CP, which meant that $\cdot\text{O}_2^-$ participated in the photocatalytic oxidation process. Nevertheless, when EDTA or IPA was added, the catalytic activities of FO/BWO (0.5) were remarkably decreased, which indicated that $\cdot\text{OH}$ and h^+ were the main active substances in the catalytic process.

The edge of the CB and VB of a semiconductor could be calculated by the following two equations: $E_{\text{CB}} = X - E_e - 0.5E_g$, where X is the absolute electronegativity of FO and BWO, E_g is the band gap energy, and E_e is the energy of the free electrons (4.5 eV) on the hydrogen scale. According to the data of the UV-vis

Fig. 10. EIS Nyquist plots of FO, BWO and FO/BWO (0.5) composite.

Fig. 11. Comparison of the effect of different radical scavengers during photocatalytic degradation of MB over FO/BWO (0.5) composite under visible light irradiation ($\lambda \geq 400$ nm).

DRS measured above, the band gap energies of BWO and FO were about 2.95 and 2.1 eV, respectively. The results revealed that the CB positions of BWO and FO were 0.40 and -0.77 eV, and the VB positions of BWO and FO were 3.35 and 1.33 eV, respectively, which were consistent with the previous research results. According to the trapping experiment results, $\cdot\text{O}_2^-$, $\cdot\text{OH}$, and h^+ all participated in the photocatalytic oxidation process. As the CB potential of BWO was more positive than the standard reduction potential of $\text{O}_2/\cdot\text{O}_2^-$ ($+0.18$ eV vs NHE), only the photoinduced electrons from the CB of FO were able to directly produce $\cdot\text{O}_2^-$. Because the VB potential of FO was much lower than the standard oxidation potential of $\text{OH}^-/\cdot\text{OH}$ ($+2.4$ eV vs NHE), $\cdot\text{OH}$ was produced by the photoinduced holes from the VB of BWO and the Fenton reaction [73,74]. The S-scheme heterojunction photocatalyst was formed between FO (reduction photocatalyst) and BWO (oxidation photocatalyst). As a reduction photocatalyst, FO displayed a relatively higher CB. In contrast, BWO as an oxidation catalyst exhibited a comparatively lower CB. When FO and BWO made contact, the electrons in BWO would be transferred to FO through their interface. An internal electric field in the direction from BWO to FO would be built. Useful holes in the VB of BWO and useful electrons in the CB of FO were retained owing to the presence of the internal electric field. Finally, photocatalytic oxidation and a reduction reaction were initiated by holes in the VB of BWO and electrons in the CB of FO [48,50].

Based on the above-mentioned results, a possible photocatalytic S-scheme mechanism for photocatalytic degradation of MB over FO/BWO composites was proposed. As shown in Fig. 12, the photoexcited electrons in FO and BWO moved from VB to CB under visible-light irradiation, which left holes in their VBs. After FO and BWO were combined, an internal electric field was formed between FO and BWO. The relatively useless photoinduced electrons in the CB of BWO migrated to the VB of FO through the intimate interface and recombined with relatively useless holes under the driving force of the built-in electronic field [48–50,75]. As a result, the photogenerated electron-holes were spatially separated, leading to the accumulation of holes in the VB of BWO and electrons in the CB of FO. The electrons on the CB of FO captured the adsorbed O_2 to form

Fig. 12. Schematic diagram of the photocatalytic oxidation of MB over FO/BWO (0.5) under visible-light irradiation ($\lambda \geq 400$ nm).

$\bullet\text{O}_2^-$, while the holes on the VB of BWO would react with OH^- to produce $\bullet\text{OH}$. In addition, the electrons in the CB of FO converted Fe^{3+} to Fe^{2+} , while the reductant Fe^{2+} reacted with H_2O_2 to form $\bullet\text{OH}$ and Fe^{3+} , which participated in the capture and decomposition of dye molecules. Consequently, MB was decomposed under the action of $\bullet\text{OH}$, $\bullet\text{O}_2^-$, and h^+ , which was consistent with the results of previous trapping experiments. The proposed charge photogenerated electron-hole transfer process could be expressed by Eqs. (1)–(8). In summary, the photo-Fenton reaction promoted the reduction of Fe^{3+} and increased the concentration of Fe^{2+} . In the meantime, the Fenton reaction also promoted the separation rate of photogenerated electron-hole pairs and improved photocatalytic activity. In addition, the construction of a 2D/2D S-scheme-system heterostructure enhanced the separation rate of the photogenerated carriers, producing abundant active sites and reducing the charge transport time and distance owing to the large contact surface between FO and BWO, which increased the photo-Fenton catalytic activities of FO/BWO photocatalysts.

4. Conclusions

2D/2D S-scheme FO/BWO composites with different mass fractions of FO were successfully prepared by a facile hydrothermal synthesis method. By combining the heterogeneous Fenton reaction with the photocatalytic process in the photo-Fenton reaction, the composite achieved preferable catalytic activity. The result of degradation experiments indicated that

FO/BWO photocatalysts combined with the heterogeneous Fenton reaction displayed superior photo-Fenton catalytic activities compared to FO, BWO, and FO/BWO catalysts without H_2O_2 . Among all the photocatalysts, FO/BWO (0.5) displayed the optimum photo-Fenton catalytic activity for the degradation of MB. The improvement of photo-Fenton catalytic activity could be attributed to the formation of a photo-Fenton system and the construction of a 2D/2D S-scheme-system heterojunction structure, which produced additional $\bullet\text{OH}$ through the photo-Fenton reaction, the contact surface between FO and BWO, produced abundant active sites, and enhanced the separation rate of photogenerated carriers. The possible catalytic mechanism of FO/BWO was proposed by active species trapping experiments. Compared with the traditional Fenton system, the degradation rate of organic dyes was considerably improved by the photo-Fenton system, which worked through $\bullet\text{O}_2^-$, $\bullet\text{OH}$, and h^+ . In addition, FO/BWO displayed stable recyclability, which highlighted its potential for industrial applications. Consequently, this work provided a facile method for the design and study of an effective 2D/2D S-scheme photo-Fenton catalyst, which displayed great potential in the removal of organic pollutants.

References

- [1] J. L. Olloqui-Sariego, G. S. Zakharova, A. A. Poloznikov, J. J. Calvente, D. M. Hushpulian, L. Gorton, R. Andreu, *ACS Catal.*, **2016**, 6, 7452–7457.
- [2] Z. L. Dong, L. Z. Feng, Y. Chao, Y. Hao, M. C. Chen, F. Gong, X. Han, R. Zhang, L. Cheng, Z. Liu, *Nano Lett.*, **2019**, 19, 805–815.
- [3] S. Bang, S. Park, Y. M. Lee, S. Hong, K. B. Cho, W. Nam, *Angew. Chem. Int. Ed.*, **2014**, 53, 7843–7847.
- [4] J. Wang, Z. F. Cao, H. S. Ren, C. Yu, S. Wang, L. Q. Li, H. Zhong, *Appl. Surf. Sci.*, **2020**, 500, 144045.
- [5] Y. Liu, Y. Y. Mao, X. X. Tang, Y. Xu, C. C. Li, F. Li, *Chin. J. Catal.*, **2017**, 38, 1726–1735.
- [6] H. Ye, Y. Liu, S. Chen, H. Wang, Z. Liu, Z. Wu, *Chin. J. Catal.*, **2019**, 40, 631–637.
- [7] C. Y. Zou, Z. D. Meng, W. C. Ji, S. Q. Liu, Z. M. Shen, Y. Zhang, N. S. Jiang, *Chin. J. Catal.*, **2018**, 39, 1051–1059.
- [8] M. J. Chen, W. Chu, J. Z. Beiyuan, Y. Huang, *Chin. J. Catal.*, **2018**, 39, 701–709.
- [9] A. Q. Wang, Z. Chen, Z. K. Zheng, H. Xu, H. Wang, K. Hu, K. Yan, *Chem. Eng. J.*, **2020**, 379, 122340.
- [10] S. Sahar, A. Zeb, Y. N. Liu, N. Ullah, A. W. Xu, *Chin. J. Catal.*, **2017**, 38, 2110–2119.
- [11] H. X. Chen, J. Zeng, M. D. Chen, Z. G. Chen, M. X. Ji, J. Z. Zhao, J. X. Xia, H. M. Li, *Chin. J. Catal.*, **2019**, 40, 744–754.
- [12] P. Soriano-Molina, J. L. Garcia Sanchez, S. Malato, P. Plaza-Bolanos, A. Agüera, J. A. Sanchez, *Appl. Catal. B*, **2019**, 256, 117801.
- [13] Q. Q. Li, M. F. Lu, W. L. Wang, W. L. Zhao, G. Q. Chen, H. F. Shi, *Appl. Surf. Sci.*, **2019**, 26, 144182.
- [14] Z. L. Du, K. J. Li, S. X. Zhou, X. Y. Liu, Y. Yu, Y. H. Zhang, Y. D. He, Y. J. Zhang, *Chem. Eng. J.*, **2020**, 380, 122427.
- [15] F. Wang, L. Song, Y. Teng, J. Xia, Z. Y. Xu, W. P. Wang, *RSC Adv.*, **2019**, 9, 35372–35383.
- [16] M. F. Lu, Q. Q. Li, C. L. Zhang, X. X. Fan, L. Li, Y. M. Dong, G. Q. Chen, H. F. Shi, *Carbon*, **2020**, 160, 342–352.
- [17] X. L. Yu, J. Q. Liu, W. C. Yin, T. Wang, L. Quan, Y. Ran, J. Y. Cui, L. Wang, Y. H. Zhang, *Appl. Surf. Sci.*, **2019**, 492, 264–271.

Graphical Abstract

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2D/2D step-scheme $\alpha\text{-Fe}_2\text{O}_3/\text{Bi}_2\text{WO}_6$ photocatalyst with efficient charge transfer for enhanced photo-Fenton catalytic activity

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The 2D/2D step-scheme $\alpha\text{-Fe}_2\text{O}_3/\text{Bi}_2\text{WO}_6$ composite with efficient charge transfer, large contact surface and abundant active sites displayed a remarkably enhanced photo-Fenton catalytic activity in the degradation of organic dyes.

- [18] S. Vignesh, S. Suganthi, J. K. Sundar, V. Raj, *Appl. Surf. Sci.*, **2019**, 488, 763–777.
- [19] L. Zhou, J. Y. Lei, L. Z. Wang, Y. D. Liu, J. L. Zhang, *Appl. Catal. B*, **2018**, 237, 1160–1167.
- [20] H. F. Shi, X. L. Huang, H. M. Tian, J. Lv, Z. S. Li, J. H. Ye, Z. G. Zou, *J. Phys. D: Appl. Phys.*, **2009**, 42, 125402.
- [21] T. Liu, L. M. Li, L. Y. Zhang, B. Cheng, W. You, J. G. Yu, *J. Power Sources*, **2019**, 426, 266–274.
- [22] H. F. Shi, C. L. Zhang, C. P. Zhou, G. Q. Chen, *RSC Adv.*, **2015**, 5, 93615–93622.
- [23] J. Li, D. D. Wu, J. Iocozzia, H. W. Du, X. Q. Liu, Y. P. Yuan, W. Zhou, Z. Li, Z. M. Xue, Z. Q. Lin, *Angew. Chem. Int. Ed.*, **2019**, 58, 1985–1989.
- [24] G. Q. Li, Q. Y. Shen, Z. Z. Yang, S. W. Kou, F. Zhang, W. F. Zhang, H. Z. Guo, Y. G. Du, *Appl. Catal. B*, **2019**, 248, 115–119.
- [25] H. F. Shi, G. Q. Chen, Z. G. Zou, *Appl. Catal. B*, **2014**, 156, 378–384.
- [26] J. X. Low, B. Z. Dai, T. Tong, C. J. Jiang, J. G. Yu, *Adv. Mater.*, **2019**, 31, 1802981.
- [27] M. F. Lu, Q. Q. Li, C. P. Zhou, C. L. Zhang, H. F. Shi, *Mater. Res. Express*, **2018**, 5, 025515.
- [28] Y. M. Zhang, N. S. Zhang, T. T. Wang, H. T. Huang, Y. Chen, Z. S. Li, Z. G. Zou, *Appl. Catal. B*, **2019**, 245, 410–419.
- [29] J. Y. Feng, H. T. Huang, T. Fang, X. Wang, S. C. Yan, W. J. Luo, T. Yu, Y. X. Zhao, Z. S. Li, Z. G. Zou, *Adv. Funct. Mater.*, **2019**, 29, 1808389.
- [30] X. H. Li, J. J. Zhang, X. Y. Zhu, J. G. Yu, K. Fan, *Appl. Surf. Sci.*, **2018**, 462, 598–605.
- [31] H. F. Shi, G. Q. Chen, C. L. Zhang, Z. G. Zou, *ACS Catal.*, **2014**, 4, 3637–3643.
- [32] Y. F. Hu, Y. Q. Wu, J. Y. Feng, H. T. Huang, C. C. Zhang, Q. F. Qian, T. Fang, J. Xu, P. Wang, Z. S. Li, Z. G. Zou, *J. Mater. Chem. A*, **2018**, 6, 2568–2576.
- [33] M. F. Lu, W. L. Wang, W. L. Zhao, Q. Q. Li, C. X. Du, J. W. Xu, X. X. Fan, H. F. Shi, *J. Phys. D: Appl. Phys.*, **2019**, 52, 095501.
- [34] G. M. Huang, S. Z. Li, L. J. Liu, L. F. Zhu, Q. Wang, *Appl. Surf. Sci.*, **2020**, 503, 144183.
- [35] Y. Zheng, X. Zhang, J. Zhao, P. Yang, *Appl. Surf. Sci.*, **2018**, 430, 585–594.
- [36] J. J. Xu, J. P. Yue, J. F. Niu, M. D. Chen, F. Teng, *Chin. J. Catal.*, **2018**, 39, 1910–1918.
- [37] G. Q. Shen, L. Pan, Z. Lü, C. Q. Wang, F. E. Aleem, X. W. Zhang, J. J. Zou, *Chin. J. Catal.*, **2018**, 39, 920–928.
- [38] J. Cheng, Y. Shen, K. Chen, X. Wang, Y. F. Guo, X. J. Zhou, R. B. Bai, *Chin. J. Catal.*, **2018**, 39, 810–820.
- [39] X. B. Li, J. Xiong, Y. Xu, Z. J. Feng, J. T. Huang, *Chin. J. Catal.*, **2019**, 40, 424–433.
- [40] S. Y. Dong, X. H. Ding, T. Guo, X. P. Yue, X. Han, J. H. Sun, *Chem. Eng. J.*, **2017**, 316, 778–789.
- [41] H. Li, F. Deng, Y. Zheng, L. Hua, C. H. Qu, X. B. Luo, *Environ. Sci. Nano*, **2019**, 6, 3670–3683.
- [42] M. L. Zhang, L. Yang, Y. J. Wang, L. F. Li, S. F. Chen, *Appl. Surf. Sci.*, **2019**, 489, 631–638.
- [43] K. Wang, Y. Li, J. Li, G. K. Zhang, *Appl. Catal. B*, **2020**, 263, 117730.
- [44] W. Guo, K. Fan, J. J. Zhang, C. J. Xu, *Appl. Surf. Sci.*, **2018**, 447, 125–134.
- [45] Y. J. Yuan, Z. K. Shen, S. T. Wu, Y. B. Su, L. Pei, Z. G. Ji, M. Y. Ding, W. F. Bai, Y. F. Chen, Z. T. Yu, Z. G. Zou, *Appl. Catal. B*, **2019**, 246, 120–128.
- [46] J. Wang, Q. Zhang, F. Deng, X. B. Luo, D. D. Dionysiou, *Chem. Eng. J.*, **2020**, 379, 122264.
- [47] R. Wang, J. Shen, W. J. Zhang, Q. Q. Liu, M. Y. Zhang, Zulfiqar, H. Tang, *Ceram. Int.*, **2020**, 46, 23–30.
- [48] F. He, A. Y. Meng, B. Cheng, W. K. Ho, J. G. Yu, *Chin. J. Catal.*, **2020**, 41, 9–20.
- [49] F. F. Mei, Z. Li, K. Dai, J. F. Zhang, C. H. Liang, *Chin. J. Catal.*, **2020**, 41, 41–49.
- [50] J. W. Fu, Q. L. Xu, J. X. Low, C. J. Jiang, J. G. Yu, *Appl. Catal. B*, **2019**, 243, 556–565.
- [51] J. L. Li, Y. X. Zhao, M. Y. Xia, H. An, H. C. Bai, J. J. Wei, B. L. Yang, G. D. Yang, *Appl. Catal. B*, **2020**, 261, 118224.
- [52] C. J. Chang, J. K. Chen, K. S. Lin, Y. H. Wei, P. Y. Chao, C. Y. Huang, *J. Alloys Compd.*, **2020**, 813, 152186.
- [53] H. Yi, M. Yan, D. L. Huang, G. M. Zeng, C. Lai, M. F. Li, X. Q. Huo, L. Qin, S. Y. Liu, X. G. Liu, B. S. Li, H. Wang, M. C. Shen, Y. K. Fu, X. Y. Guo, *Appl. Catal. B*, **2019**, 250, 52–62.
- [54] J. D. Hu, D. Y. Chen, Z. Mo, N. J. Li, Q. F. Xu, H. Li, J. H. He, H. Xu, J. M. Lu, *Angew. Chem. Int. Ed.*, **2019**, 58, 2073–2077.
- [55] S. W. Cao, B. J. Shen, T. Tong, J. W. Fu, J. G. Yu, *Adv. Funct. Mater.*, **2018**, 28, 1800136.
- [56] C. Y. Jin, Z. L. Li, Y. Zhang, M. Wang, Z. M. Wu, Y. H. Xie, Y. Z. Wang,

- T. Zhu, *Sep. Purif. Technol.*, **2019**, 224, 33–43.
- [57] Z. Wang, L. Wang, *Chin. J. Catal.*, **2018**, 39, 369–378.
- [58] B. S. Li, C. Lai, G. M. Zeng, L. Qin, H. Yi, D. L. Huang, C. Y. Zhou, X. G. Liu, M. Cheng, P. Xu, C. Zhang, F. L. Huang, S. Y. Liu, *ACS Appl. Mater. Interfaces*, **2018**, 10, 18824–18836.
- [59] C. Jaramillo-Páez, J. A. Navío, M. C. Hidalgo, A. Bouzianib, M. E-Azzouzi, *J. Photochem. Photobiol. A*, **2017**, 332, 521–533.
- [60] J. Q. Li, Z. X. Liu, Z. F. Zhu, *Appl. Surf. Sci.*, **2014**, 320, 146–153.
- [61] T. P. Xie, Y. Liu, H. A. Wang, Z. B. Wu, *Sci. Rep.*, **2019**, 9, 7551.
- [62] Z. X. Lin, J. M. Gong, P. Fu, *J. Mater. Sci.: Mater. Electron.*, **2017**, 28, 4424–4430.
- [63] R. Chen, J. Lu, J. Xiao, C. Z. Zhu, S. C. Peng, T. H. Chen, *Solid State Sci.*, **2017**, 71, 14–21.
- [64] Y. D. Guo, G. K. Zhang, J. Liu, Y. L. Zhang, *RSC Adv.*, **2013**, 3, 2963–2970.
- [65] J. J. Wang, L. Tang, G. M. Zeng, Y. C. Deng, Y. N. Liu, L. L. Wang, Y. Y. Zhou, Z. Guo, J. J. Wang, C. Zhang, *Appl. Catal. B*, **2017**, 209, 285–294.
- [66] X. N. Liu, Q. F. Lu, C. Q. Wang, *Mater. Lett.*, **2015**, 154, 81–84.
- [67] Q. S. Wu, Y. Feng, G. Y. Zhang, Y. Q. Sun, Y. Y. Sun, D. Z. Gao, *Mater. Res. Bull.*, **2014**, 49, 440–447.
- [68] X. N. Liu, Q. F. Lu, C. F. Zhu, S. W. Liu, *RSC Adv.*, **2014**, 5, 4077–4082.
- [69] S. Adhikari, S. Selvarai, D. H. Kim, *Appl. Catal. B*, **2019**, 244, 11–24.
- [70] S. Y. Wang, H. Yang, Z. Yi, X. X. Wang, *J. Environ. Manag.*, **2019**, 248, 109341.
- [71] S. S. Zhu, X. F. Zou, Y. Zhou, Y. J. Zeng, Y. Long, Z. F. Yuan, Q. B. Wu, M. Li, Y. Z. Wang, B. Xiang, *J. Alloys Compd.*, **2019**, 775, 63–71.
- [72] X. H. Jia, C. D. Cheng, S. W. Yu, J. Yang, Y. Li, H. J. Song, *Sens. Actuators B*, **2019**, 300, 127012.
- [73] J. J. Chi, S. D. Li, F. M. Wang, L. N. Gao, Y. M. Li, X. R. Zhang, J. Lu, *Dalton Trans.*, **2019**, 48, 3327–3337.
- [74] H. N. Che, G. B. Che, H. J. Dong, W. Hu, C. B. Liu, C. M. Li, *Appl. Surf. Sci.*, **2018**, 455, 705–716.
- [75] H. N. Ge, F. Y. Xu, B. Cheng, J. G. Yu, W. K. Ho, *ChemCatChem*, **2019**, 11, 6301–6309.

具有高效电荷分离的2D/2D α -Fe₂O₃/Bi₂WO₆ S型异质结增强光-芬顿催化活性

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摘要: 近年来, Fenton反应由于其成本低, 反应速度快, 操作简单等优势受到了广泛的研究. 传统的均相Fenton反应可通过H₂O₂氧化Fe²⁺产生具有强氧化性的羟基自由基, 用于处理难降解的有机物. 然而, Fenton反应存在两个主要问题, 首先, 在Fenton反应中需要加入大量的酸来维持酸性环境, 以保证反应的最佳活性. 其次, Fenton反应中铁离子不断流失并形成固体污泥, 这严重影响了Fenton反应产生•OH的效率. 目前, 将光催化反应与非均相芬顿反应相结合是改善这些问题的有效方案. 非均相光芬顿反应不仅能提高有机物降解的活性, 而且通过光催化剂导带上的电子有效减少Fe³⁺的浸出和铁氢氧化物沉淀的产生.

最近, 作为一种可见光Fenton催化剂, α -Fe₂O₃可以在几乎中性的条件下发生光芬顿反应, 这解决了在反应过程中需要随时调整PH值的问题. 此外, 光照条件下 α -Fe₂O₃价带上的电子能跃迁至导带并将Fe³⁺还原成Fe²⁺, 从而减少铁离子的损耗. 然而, 由于光生载流子复合率较高等问题, 单一 α -Fe₂O₃光催化剂的催化活性仍不理想. 构建具有2D/2D结构的S型异质结可以缩短电子在界面间的传输距离, 增大材料的活性位点, 将光生电子-空穴在空间上分离, 从而有效增强光生载流子的分离效率. 因此, 构建2D/2D α -Fe₂O₃/Bi₂WO₆ S型异质结, 并用于光芬顿反应有望进一步提高对有机污染物的降解效率.

本文通过简易的水热法制备了具有2D/2D结构的 α -Fe₂O₃/Bi₂WO₆ S型异质结光芬顿催化剂, 并通过XRD、BET、TEM、XPS和UV-Vis等手段对催化剂的晶体结构、元素状态、微观结构、光学性质和化学组分进行了表征. 通过在可见光照射下降解甲基蓝(MB), 考察了 α -Fe₂O₃/Bi₂WO₆的光芬顿催化活性. 结果表明, 由于光催化反应与Fenton反应的协同作用, α -Fe₂O₃/Bi₂WO₆表现出了明显增强的光-Fenton催化活性, 最佳比例的 α -Fe₂O₃/Bi₂WO₆的活性分别是单一 α -Fe₂O₃和Bi₂WO₆的11.06倍和3.29倍. 本文将光催化反应与Fenton反应相结合, 一方面, 光催化反应对Fe³⁺的还原有促进作用, 提高了Fe²⁺的浓度, 从而提升羟基自由基的产量; 另一方面, Fenton反应对 α -Fe₂O₃/Bi₂WO₆中电子的利用阻止了光生载流子的复合, 进一步提高了光催化降解效率. 此外, 由于二维纳米片之间具有更大的接触面积, 2D/2D异质结可以缩短电荷传输时间和距离, 促进了光生电子-空穴的分离. 同时, 具有较大比表面积的2D/2D材料可以在催化剂表面提供大量用于有机物氧化分解的活性位点. 而S型异质结的构建不但促进了界面电荷的转移和分离, 还能维持最佳的电荷氧化还原电位, 这都提升了催化剂的光芬顿催化活性. 总之, 本文为合成可高效降解有机污染物的非均相光-芬顿催化剂提供了新的思路.

关键词: Bi₂WO₆; α -Fe₂O₃; S型异质结; 光芬顿; 2D光催化剂

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