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2D/2D type-II $\text{Cu}_2\text{ZnSnS}_4/\text{Bi}_2\text{WO}_6$ heterojunctions to promote visible-light-driven photo-Fenton catalytic activity

Li Guo, Kailai Zhang, Xuanxuan Han, Qiang Zhao, Yuanyuan Zhang, Mian Qi, Danjun Wang*, Feng Fu[#]

Shaanxi Key Laboratory of Chemical Reaction Engineering, College of Chemistry & Chemical Engineering, Yan'an University, Yan'an 716000, Shaanxi, China

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ABSTRACT

In this work, a set of novel $\text{Cu}_2\text{ZnSnS}_4/\text{Bi}_2\text{WO}_6$ (CZTS/BWO) two-dimensional (2D)/two-dimensional (2D) type-II heterojunctions with different CZTS weight ratios (1%, 2%, and 5%) were successfully synthesized via a brief secondary solvothermal process. The successful formation of the heterojunctions was affirmed by characterization methods such as X-ray photoelectron spectroscopy and high-resolution transmission electron microscopy. The photocatalytic activity results showed that the prepared CZTS/BWO heterojunctions had excellent photocatalytic behaviors for organic degradation, especially when the mass fraction of CZTS with respect to BWO in the composite was 2%. Moreover, the addition of hydrogen peroxide (H_2O_2) could further improve the dye and antibiotic degradation efficiencies. The reinforced photocatalytic and photo-Fenton degradation performance were primarily attributable to the introduction of BWO, which afforded increased active sites, expanded the solar spectral response range, and accelerated the cycle of $\text{Cu(II)}/\text{Cu(I)}$; after four cycling times, its catalytic activity did not decrease significantly. In addition, reasonable hypotheses of the photocatalytic and photo-Fenton catalytic mechanisms were formulated. This study is expected to provide a visual approach for designing a novel photo-Fenton catalyst to jointly utilize the photocatalytic and Fenton activities, which can be better applied to the purification of residual organics in wastewater.

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1. Introduction

Advanced oxidation processes (AOPs) have proved to be very attractive procedures to treat organic pollutants [1–7]. Since Fenton et al. [8] discovered the strong ability of an $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ system to catalyze oxidative tartaric acid, a great deal of research work has focused on the degradation of organ-

ic pollutants by the Fenton reaction [9–12]. Nevertheless, owing to the narrow pH range, pretreatment must be carried out during the Fenton reaction. Meanwhile, the iron sludge generated after the reaction demands further treatment to meet the emission requirements, thus restricting the development of the Fenton reaction to degrade organic pollutants [13,14]. Lately, it has been confirmed that semiconductor photocatalytic materi-

* Corresponding author. Tel: +86-911-2332037; E-mail: wangdj761118@163.com

[#] Corresponding author. Tel: +86-911-2332003; E-mail: yadxufeng@126.com

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als and various iron-based and copper-based Fenton materials form photo-Fenton systems, which can solve the circulation problem of high-valence metal ions to low-valence metal ions in the Fenton reaction [15].

As another AOP, photocatalysis is being developed, having the advantages of green products, mild reaction conditions, simple operation, and good selectivity. In 1972, Fujishima et al. [16] discovered for the first time that the n-type semiconductor, TiO_2 , could catalyze the decomposition of water to produce H_2 under illumination. From then on, photocatalysis has unveiled the prologue. During the past few decades, research on photocatalytic degradation of organic pollutants has developed rapidly and become a leading technology in wastewater treatment [17–19]. Because the band gap (E_g) of the metal oxide catalyst, TiO_2 , is relatively large (about 3.2 eV), it can only absorb ultraviolet light with a wavelength less than or equal to 400 nm [20]. However, infrared and visible lights are the most abundant in the solar light, therefore the above limits the possibility of large-scale popularization and application of TiO_2 . In order to fully utilize the potential advantages of both the Fenton oxidation technology and photocatalysis in degrading organic pollutants, it is vital to construct new catalysts that can respond to a wide solar spectrum to induce visible-light-responsive photo-Fenton catalysis.

As one of the most investigated perovskite-type oxides owing to the distinctive layered structure and outstanding performance in the photodegradation of organics, Bi_2WO_6 (BWO) has a relatively wide band gap of 2.6–2.8 eV, which can respond to a part of visible light [21–24]. However, the practical application of Bi_2WO_6 is still hindered by the high recombination rate of its photo-generated electron-hole pairs and narrow light-responsive region. To this end, many modification strategies have been developed to efficiently utilize the solar energy and promote its activity [25–29]. Among these strategies, coupling Bi_2WO_6 with suitable cocatalysts to fabricate heterojunctions is proven to be an effective strategy for promoting the separation of the photogenerated carriers and broadening the light-responsive region [30–32]. Among them, $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) is a narrow band-gap semiconductor, which can respond to visible light and even near-infrared light. Recently, it has been widely reported that CZTS can be an effective cocatalyst that can be combined with other semiconductors to increase the photocatalytic activity [33,34].

In this study, two-dimensional/two-dimensional (2D/2D) type-II p-n CZTS/BWO heterojunctions were fabricated by a second solvothermal method. The photocatalytic and photo-Fenton catalytic activities were evaluated using azo dye rhodamine B (RhB) and colorless tetracycline hydrochloride (TC-HCl) as the simulated organic pollutants under visible-light irradiation. On the basis of the energy band analysis and electron spin resonance (ESR), the possible photocatalytic and photo-Fenton catalytic mechanisms were proposed. The combination of the photocatalytic and Fenton reactions could enable full utilization of their respective complementary advantages and rapidly degrade pollutants under mild conditions.

2. Experimental

2.1. Chemicals

Sodium hydroxide (NaOH, 96.0%), zinc acetate dihydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, 99.0%), and cetyltrimethylammonium bromide ($\text{C}_{19}\text{H}_{42}\text{BrN}$, 99.0%) were purchased from Tianjin Kemio Chemical Reagent Co., Ltd (Tianjin, China). Sodium tungstate dihydrate ($\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$, 99.5%), bismuth nitrate pentahydrate ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, 99%), and anhydrous ethanol ($\text{C}_2\text{H}_5\text{OH}$, 99.7%) were purchased from Tianjin Zhiyuan Chemical Reagent Co., Ltd (Tianjin, China). Hydrochloric acid (HCl, 36%), nitric acid (HNO_3 , 63%), and ammonia solution ($\text{NH}_3 \cdot \text{H}_2\text{O}$, 28%) were purchased from Sichuan Xilong Chemical Co., Ltd (Sichuan, China). Thiourea ($\text{CH}_4\text{N}_2\text{S}$, 99.0%) was purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Hydrated stannic chloride ($\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$, 99.0%) was purchased from Shanghai Aladdin Biochemical Technology Co., Ltd (Shanghai, China). Copper(II) acetate monohydrate ($\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$, 99.0%) and TC-HCl ($\text{C}_{22}\text{H}_{24}\text{N}_2\text{O}_8 \cdot \text{HCl}$, biotechnology level) were purchased from Shanghai Macklin Biochemical Co., Ltd (Shanghai, China). Rhodamine B ($\text{C}_{28}\text{H}_{31}\text{ClN}_2\text{O}_3$, Analytical grade) was purchased from Tianjin Tianxin Fine Chemical Development Center (Tianjin, China). Deionized water was used as a solvent. All the reagents were of analytical grade, except TC-HCl, and were used without any further purification.

2.2. Sample preparation

2.2.1. Preparation of Bi_2WO_6 (BWO) nanosheets

BWO nanosheets were synthesized by an improved hydrothermal method according to a previous report [35]. Firstly, 1.94 g of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ was completely dissolved in 5 mL of 4 mol/L HNO_3 under stirring for 30 min. Afterward, 0.20 g of cetyltriethylammonium bromide (CTAB) was dissolved in 300 mL of deionized water and 6.0 g of $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ was dissolved in 200 mL of deionized water to obtain homogeneous solutions, respectively. Then, 30 mL of the CTAB and 20 mL of the $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ aqueous solutions were added to the above mixture in turn. After the addition, the pH was adjusted by adding a diluent of neutralized ammonia water and deionized water in a ratio of 1:1 drop by drop until the pH was neutral. Following continuous stirring for 1 h, it was transferred to a 100-mL Teflon-lined stainless-steel autoclave and put it into an oven, reacting for 14 h at 180 °C. Finally, the resultant was taken out to wash and dry and was put it into a muffle furnace, calcining for 3 h at 300 °C. The obtained sample was denoted as BWO.

2.2.2. Preparation of 2D/2D $\text{Cu}_2\text{ZnSnS}_4/\text{Bi}_2\text{WO}_6$ (CZTS/BWO) heterojunctions

The 2D/2D CZTS/BWO heterojunctions were prepared by an in situ assembling strategy [34]. In a typical process, 0.0128 g of $\text{CH}_4\text{N}_2\text{S}$, 0.0134 g of $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$, 0.0118 g of $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$, and 0.0074 g of $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ were fully dissolved in 70 mL of anhydrous ethanol. Subsequently, 1.5 g of Bi_2WO_6 was added, and the mixture was stirred for 1 h. The mixture was transferred to a 100-mL Teflon-lined stain-

less-steel autoclave and placed in an oven to react at 200 °C for 24 h. Once taken out, the obtained products were washed with ethanol and deionized water and finally dried at 60 °C for 8 h. This resulted in the 1.0% CZTS/BWO heterojunction. According to this method, we could sequentially prepare CZTS/BWO heterojunctions with different percentages of CZTS based on the 1.0% CZTS/BWO. The contents of $\text{CH}_4\text{N}_2\text{S}$, $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$, $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$, and $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ were changed according to the required percentages, and the obtained samples were denoted as $x\%$ CZTS/BWO ($x = 2$ and 5, respectively). Moreover, pure CZTS was prepared under the same conditions, except for the addition of BWO, for comparison.

2.3. Characterization of as-prepared samples

An X-ray powder diffractometer (Shimadzu XRD-7000) was used to analyze the crystallographic properties of the catalysts. X-ray photoelectron spectroscopy (XPS) was performed with a PHI-5400 (America PE) 250 xi system. The morphology of the samples was analyzed via scanning electron microscopy (SEM, JSM-6700F) and transmission electron microscopy (TEM, JEM-2100) (Japan electronics). Energy dispersive X-ray (EDX) was performed via field-emission scanning electron microscopy (FESEM, JSM-7610F) to analyze the elemental features of the samples. The UV-Vis diffuse reflectance spectra (UV-Vis-DRS) were measured on a UV-2550 UV-Vis spectrophotometer. The ESR spectra were examined on a Bruker ELEXSYS-II E500 CW-EPR model. Time-resolved photoluminescence (TR-PL) spectra were obtained by a FLS920 fluorescence spectrometer (Edinburgh Analytical Instruments, UK).

2.4. Photocatalytic and photo-Fenton catalytic activity measurements

Typically, 20 mg/L azo dye RhB and 40 mg/L colorless TC-HCl were degraded in the presence or absence of visible light and H_2O_2 at room temperature. The experimental processes were as follows: 0.02 g catalyst was added to a 50 mL-quartz tube, and then 20 mL of simulated contaminant aqueous solution was pipetted into the tube. At the same time, a circulating cooling water was introduced to avoid the influence of temperature. Before the photocatalytic reaction, the mixture was stirred in the dark to reach the adsorption/desorption equilibrium, and then a certain amount of H_2O_2 was added before turning on a 300-W metal halide lamp with a 420-nm cut-off filter as the visible light source. Irradiation was introduced, and 3 mL of the reaction liquid was taken out at a certain time interval and centrifuged to obtain the supernatants for UV analysis at 554 and 357 nm of the maximum absorption peaks of RhB and TC-HCl, respectively.

3. Results and discussion

3.1. Structure and physical properties of samples

XRD was employed to investigate the phase structures of the prepared samples. Fig. 1 shows the XRD patterns of CZTS,

Fig. 1. X-ray powder diffraction (XRD) patterns of the as-synthesized CZTS, BWO, and 2% CZTS/BWO heterojunction.

BWO, and the 2% CZTS/BWO heterojunction, respectively. The diffraction peaks of BWO at 28.30° (131), 32.67° (060), 32.79° (200), 32.91° (002), 47.14° (202), 55.66° (191), 58.53° (262), 76.07° (193), and 78.53° (204) can be indexed to an orthorhombic system (JCPDS no. 39-0256) [36]. However, the crystallinity of CZTS is relatively lower than that of BWO. The two characteristic peaks corresponding to (112) and (220) observed at 28.5° and 47.3° can be considered as kesterite CZTS (JCPDS no. 26-0575) [34]. The prepared 2% CZTS/BWO heterojunction shows the homoplastic crystal structure of BWO, and only the peak intensity is attenuated. The latter may be due to the low loading or the main two diffraction peak positions of CZTS being basically coincident with those of BWO, and its low crystallinity.

The surface composition and elemental valence of the samples were demonstrated by XPS. As can be seen from Fig. 2a, the 2% CZTS/BWO heterojunction contains Bi, W, O, C, Cu, Zn, Sn, and S elements; Bi, W, C, and O elements appear in BWO; and Cu, Zn, Sn, C, and S elements are observed in CZTS, where C 1s belongs to the pollution of the instrument itself. Fig. 2b–g show the high-resolution XPS spectra of Bi 4f, W 4f, Cu 2p, Zn 2p, Sn 3d, and S 2p. The characteristic peaks of the 2% CZTS/BWO heterojunction at 164.45 and 159.17 eV showing a shift to a higher binding energy compared to those in BWO corresponding to Bi 4f_{5/2} and Bi 4f_{7/2} signify that the Bi element is in a +3 state (Fig. 2b) [37]. In Fig. 2c, the characteristic peaks at 37.6 and 35.5 eV of the 2% CZTS/BWO heterojunction show a shift to a higher binding energy compared to those of BWO corresponding to W 4f_{5/2} and W 4f_{7/2}, suggesting that the W element exists in a +6 state [38]. As can be seen from Fig. 2d, the characteristic peaks of the 2% CZTS/BWO heterojunction and CZTS at 951.57 and 931.7 eV correspond to Cu 2p_{1/2} and Cu 2p_{3/2}, revealing the presence of a Cu⁺ state [34]. Fig. 2e shows that in the 2% CZTS/BWO heterojunction and CZTS XPS spectra, the Zn²⁺ state is proved by two distinct peaks at 1021.8 and 1044.8 eV with a separation of 23 eV, showing a shift to a higher binding energy compared to those in CZTS. The peaks are

Fig. 2. (a) XPS survey spectra of BWO, CZTS, and the 2% CZTS/BWO heterojunction; High-resolution spectra of (b) Bi 4f, (c) W 4f, (d) Cu 2p, (e) Zn 2p, (f) Sn 3d, and (g) S 2p of the 2% CZTS/BWO heterojunction.

attributed to Zn 2p_{3/2} and Zn 2p_{1/2}, respectively [39]. The two peaks in Fig. 2f centered at 486.6 and 495.02 eV correspond to Sn 3d_{5/2} and Sn 3d_{3/2}, show a shift to a higher binding energy compared to those in CZTS and confirm rationally that the Sn element is in an Sn⁴⁺ state [40]. As can be seen from Fig. 2g, the corresponding characteristic peaks at 164.47 and 159.18 eV are Bi 4f_{5/2} and Bi 4f_{7/2}, and no remarkable characteristic peaks of S 2p are observed. The latter may be owing to the low content of CZTS in the 2% CZTS/BWO heterojunction and close binding energy positions of S 2p and Bi 4f [41]. From Fig. 2a–g, it can be seen that CZTS nanosheets are successfully coupled with BWO nanosheets.

The morphologies and microstructures of CZTS, BWO, and the 2% CZTS/BWO heterojunction were studied by SEM, EDX mapping, TEM, and HRTEM techniques. As shown in Fig. 3a–b, BWO is remarkably observed to have a 2D nanosheet-like structure. However, Fig. 3c–d showed that CZTS exhibited a three-dimensional (3D) spherical structure. The SEM images observed in Fig. 3e–f showed that the 2D and 2D nanosheets are united together. The element distributions of CZTS and

Fig. 3. (a, b) SEM images of BWO, (c, d) CZTS and (e, f) 2% CZTS/BWO heterojunction, (g–n) EDX element mapping for the 2% CZTS/BWO heterojunction.

Fig. 4. TEM images of (a) BWO, (b) CZTS, and (c) 2% CZTS/BWO heterojunction; (d) HRTEM image of the 2% CZTS/BWO heterojunction.

BWO in the CZTS/BWO heterojunction was further determined by EDX element mapping, and the results are shown in Fig. 3g–n. Seven elements: Bi, W, O, Cu, Zn, Sn, and S are uniformly distributed on the 2% CZTS/BWO heterojunction.

Fig. 4a–d show the TEM images of BWO, CZTS, and the 2% CZTS/BWO heterojunction. Fig. 4a–b further confirm that BWO exhibits a sheet-like structure, whereas CZTS exhibits a 3D spherical structure. Fig. 4c–d display the TEM images of the 2% CZTS/BWO heterojunction, further confirming that BWO and CZTS form a 2D/2D structure. The d values of three different stripes with lattice spacings are 0.273, 0.315, and 0.313 nm, respectively, which can be assigned to the (200) and (131) planes of BWO and (112) plane of CZTS separately. The results suggest that the CZTS nanosheets are uniformly assembled onto the surface of the BWO nanosheets.

3.2. Photo-absorption characteristics of samples

As can be seen from Fig. 5, CZTS has a strong absorption in the UV-Vis light region, and BWO also exhibits a strong absorption in the visible range. It is worth noting that its response range to visible light will be red shifted to a certain extent after the CZTS/BWO heterojunction is formed, thus improving the utilization rate of visible light.

Fig. 5. UV-Vis diffuse reflectance spectra of BWO, CZTS, and the 2% CZTS/BWO heterojunction.

Fig. 6. Time-resolved fluorescence decay spectra of BWO and the 2% CZTS/BWO heterojunction. A two-exponential function equation is used to fit the decay time, $y = y_0 + A_1 \cdot e^{-x/\tau_1} + e^{-x/\tau_2}$, $\tau_{av} = (A_1 \cdot \tau_1^2 + A_2 \cdot \tau_2^2) / (A_1 \cdot \tau_1 + A_2 \cdot \tau_2)$.

3.3. Charge-carriers separation efficiency

Fig. 6 shows the time-resolved fluorescence lifetime spectra of BWO and the 2% CZTS/BWO heterojunction. We mainly observe the lifetimes of the carriers. The photoelectron lifetimes conform to the two-exponential decay model [42]. The decay times (τ_1 and τ_2) and PL aptitudes (A_1 and A_2) are given in Table 1. The 2% CZTS/BWO heterojunction (2.01 ns) exhibits an enhanced lifetime compared to BWO (0.929 ns), which indicates that the coupling of CZTS can enhance the separation of the photogenerated electron-hole pairs and ultimately improve the carrier lifetime. The enhancement of the photoelectron lifetime is very helpful to improve the catalytic performances of the photocatalytic and photo-Fenton reactions.

3.4. Photocatalytic and photo-Fenton catalytic performances

Azo dye RhB was firstly used as a simulated pollutant to evaluate the photocatalytic and photo-Fenton catalytic performances of the catalyst. Fig. 7a displays that when no photocatalyst is added, the dye concentration hardly changes after the photocatalytic reaction, which indicates that the dye molecules have a high photostability. When BWO and CZTS are used as the catalysts alone, the degradation efficiency of RhB by BWO can reach 62%, whereas CZTS has a relatively weak photocatalytic activity, reaching only 20%. The formed CZTS/BWO heterojunctions exhibits a markedly enhanced photocatalytic activity. Among them, the photocatalytic efficiency is the best when the loading of CZTS is 2%, which can reach about 94% of the degradation efficiency. Further, the increase in the CZTS content leads to a sharp decline in the photocatalytic activity.

Table 1

Parameters of the time-resolved PL decay curves.

Sample	τ_1 (ns)	A_1	τ_2 (ns)	A_2	T_{av} (ns)
BWO	0.93	2.09×10^{11}	11.52	965.62	0.929
2% CZTS/BWO	1.97	10441	23.22	1848.30	2.01

Fig. 7. (a) Photocatalytic degradation variation of RhB concentration with the irradiation time under different catalyst conditions, (b) plot of $\ln(C_0/C)$ vs. time, (c) corresponding apparent rate constants of the photocatalytic degradation, and (d) photo-Fenton catalytic degradation variation of RhB concentration with irradiation time under different catalyst conditions.

This may be because excessive CZTS loading reduces the absorption of light, which indicates that the configuration of a heterojunction is very beneficial to enhance the photocatalytic activity. The efficiency of the photocatalytic degradation of RhB was furtherly simulated by kinetic analysis using the first-order kinetic equation: $\ln(C_0/C) = k_{app} \cdot t$, as shown in Fig. 7b. Based on the comparison chart of the rate, as shown in Fig. 7c, the photocatalytic reaction rate constants (k_{app}/min^{-1}) of the 2% CZTS/BWO heterojunction are 3.04 and 12.5 folds compared to those of BWO and CZTS, respectively. Fig. 7d presents that the degradation efficiency of RhB by H_2O_2 alone can reach 13% after 50 min irradiation. However, when H_2O_2 is introduced into the photocatalytic system with photocatalyst, the degradation efficiency of 2% CZTS/BWO heterojunction and BWO can reach 76% and 62%, respectively, after 10 min of visible light illumination. The enhanced catalytic activity may be attributed to the synergistic effect of photocatalysis and Fenton catalysis.

The 2% CZTS/BWO heterojunction was selected for further photo-Fenton degradation of colorless pollutants. The results are presented in Fig. 8. It is notable from Fig. 8a that the 2% CZTS/BWO heterojunction also has a high activity performance for TC-HCl under the photo-Fenton condition compared to under BWO. At the same time, the effects of the catalyst dosage, H_2O_2 volume, and pH values on the photocatalytic activity were studied. The effect of the H_2O_2 volume on TC-HCl degradation is

shown in Fig. 8b. The degradation efficiency of TC-HCl increases from 76.4% to 92.5% with the increase in H_2O_2 from 0.05 to 1.6 mL because more $\cdot\text{OH}$ can be generated by increasing the amount of H_2O_2 . Fig. 8c displays the effect of the catalyst dosage on the degradation of TC-HCl. The degradation efficiency gradually increases as the catalyst dosage increases from 0.01 g to 0.03 g. However, as the catalyst dosage continues to increase to 0.04 g, the degradation efficiency is only slightly increased. The effect of the pH is shown in Fig. 8d. It can be seen that when the initial conditions of the pH reach neutrality, the degradation efficiency is maximized and there is a decline with the increase or decrease in the pH value. This is because neutral pH conditions may be conducive to causing the production of active radicals with a strong oxidation ability.

3.5. Stability of the catalyst

Fig. 9a shows the degradation efficiency of TC-HCl after the photo-Fenton catalytic cycle with the 2% CZTS/BWO heterojunction as the catalyst. It can be seen that the photo-Fenton activity of the heterojunction does not significantly decrease. Moreover, after repeated experiments, no significant new peaks are observed, as shown in Fig. 9b; after the XRD tests, only the intensity is slightly reduced, demonstrating the high stability of the catalyst.

Fig. 8. (a) Photo-Fenton catalytic degradation variation of the TC-HCl concentration with the prolongation of the irradiation time under different catalyst conditions, (b) effect of the initial H₂O₂ volume, (c) catalyst dosage, and (d) pH value for the photo-Fenton catalytic degradation of TC-HCl over the 2% CZTS/BWO heterojunction.

Fig. 9. (a) Degradation efficiency for TC-HCl during different cycles and (b) XRD pattern for the 2% CZTS/BWO heterojunction before and after the photo-Fenton reaction.

3.6. Photocatalytic and photo-Fenton catalytic mechanisms

To detect the main active species in the photocatalytic and photo-Fenton catalytic reactions, the ESR test was carried out, and the results are shown in Fig. 10. We mainly discuss the important roles of $\cdot\text{OH}$ and $\cdot\text{O}_2^-$ in the catalytic process. As can be seen from Fig. 10a, the characteristic for the strong ESR signals of the four characteristic peaks can be considered as $\cdot\text{OH}$,

and the 2% CZTS/BWO heterojunction can produce more $\cdot\text{OH}$ under the double action of visible light and H₂O₂ compared to BWO. Similarly, it can be deduced that in Fig. 10b, the ESR signal of the six characteristic peaks can be considered as $\cdot\text{O}_2^-$. The role of $\cdot\text{O}_2^-$ in the catalytic process is explored, and the $\cdot\text{O}_2^-$ signals of the 2% CZTS/BWO heterojunction are also significantly enhanced under the action of visible light and H₂O₂ compared to those of BWO. Therefore, the additional $\cdot\text{OH}$ and $\cdot\text{O}_2^-$ generated in the photo-Fenton oxidation process can carry

Fig. 10. DMPO spin-trapping ESR spectra of the catalysts for (a) DMPO- $\cdot$ OH and (b) DMPO- $\cdot$ O₂⁻.

out the oxidation reaction together, thereby remarkably enhancing the catalytic degradation capability of the catalyst.

Through a series of investigations, we can infer that the enhanced mechanisms of the photocatalytic and photo-Fenton reactions for the degradation of organic pollutants over the 2% CZTS/BWO heterojunction are as follows: according to the results of the UV-Vis-DRS and valence band XPS spectra, the band gap of BWO and CZTS were estimated as 2.64 and 1.52 eV, respectively (Fig. 11a–b), and the valence band maximum (VBM) was estimated as 2.22 and 1.00 eV, respectively (Fig. 11c–d). Moreover, BWO and CZTS have been widely recognized as

n-type and p-type semiconductors, respectively [43,34]. The Fermi levels (E_F) of BWO and CZTS are located near to the conduction band (CB) and valence band (VB), respectively. Accordingly, the work function (W_I) of BWO is more negative than that of CZTS (W_{II}), as depicted in Fig. 12. Upon contact, free electrons migrate from the BWO side to the CZTS side until the two semiconductors reach equal E_F values. Thus, the BWO side is positively charged, whereas the CZTS side is negatively charged at the interface. A built-in electric field (BIEF) from the BWO to CZTS forms at the interface, and the band edge bending occurs. Under light irradiation, the photogenerated electrons of

Fig. 11. Tauc plots of $(\alpha h\nu)^{1/2}$ versus $h\nu$ and valence band XPS spectra of (a,c) BWO and (b,d) CZTS.

Fig. 12. Proposed photocatalytic and photo-Fenton catalytic mechanisms by the 2D/2D CZTS/BWO type-II p-n heterojunction. W_I and W_{II} denote the work functions of BWO and CZTS, respectively. V_{ac} , CBM, VBM, and E_F stand for the vacuum level, conduction band minimum, valence band maximum, and Fermi level, respectively.

CZTS ($E_{CBM} = -0.52$ eV vs. NHE) can transfer to BWO ($E_{CBM} = -0.42$ eV vs. NHE), whereas the photogenerated holes can transfer from BWO ($E_{VBM} = 2.22$ eV vs. NHE) to CZTS ($E_{VBM} = 1.00$ eV vs. NHE) under BIEF. Accordingly, a type-II p-n junction charge carrier transfer mode is formed because of the existing BIEF.

At this time, electrons can reduce O_2 to $\cdot O_2^-$, promoting the degradation of pollutants into small molecular substances. The photogenerated holes left on the VB are positively charged and have strong oxidation properties, which can oxidize and degrade pollutants to form harmless small molecular inorganic substances, such as CO_2 and H_2O . Moreover, these holes can oxidize OH^- to form $\cdot OH$ with a strong activity to promote the oxidative degradation of pollutants. The above charge carrier transfer mode actually causes an enhancement in the separation ability of the photogenerated electron-hole pairs of BWO. In the traditional Fenton reaction, Cu(I) mainly reacts with H_2O_2 to generate Cu(II) and $\cdot OH$, but the slow conversion between Cu(I) and Cu(II) results in an unsatisfactory actual processing effect. However, the introduction of photogenerated electrons can accelerate the reduction of Cu(II) to Cu(I) and improve the utilization rate of H_2O_2 in the system to generate $\cdot OH$, thereby enhancing the ultra-strong ability to degrade pollutants. It is presumed that the mechanism of the photo-Fenton oxidation degradation of pollutants in the presence of the 2D/2D type-II p-n CZTS/BWO heterojunctions is as follows:

4. Conclusions

We designed a new 2D/2D CZTS/BWO type-II p-n heterojunction for the first time to achieve the photo-Fenton reaction. The method of hydrothermal synthesis could easily produce 2D Bi_2WO_6 nanosheets, then CZTS nanosheets were grown on the surface of the BWO nanosheets by a second solvothermal method, and finally, the heterojunction was formed. Owing to the enhanced visible light absorption capability, large charge carrier separation, and mobility exhibited by the heterojunction material, its catalytic activity was greatly enhanced. The synergistic effect between the photocatalysis and Fenton catalysis was utilized to the greatest extent to improve the photo-Fenton activity. At the same time, the ESR technique was used to study the mechanism of the photo-Fenton catalysis. It was found that $\cdot O_2^-$ and $\cdot OH$ were the main active transient species in the degradation process. At the same time, the catalyst still maintained high photo-Fenton catalytic activity after 4 cycles, indicating a relatively high photostability. The synthesized CZTS/BWO heterojunction could provide a concept to researchers to modify traditional photocatalytic materials with Cu-based semiconductor materials to realize photo-Fenton catalysis.

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Graphical Abstract

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2D/2D type-II $\text{Cu}_2\text{ZnSnS}_4/\text{Bi}_2\text{WO}_6$ heterojunctions to promote visible-light-driven photo-Fenton catalytic activityLi Guo, Kailai Zhang, Xuanxuan Han, Qiang Zhao, Yuanyuan Zhang, Mian Qi, Danjun Wang *, Feng Fu *
Yan'an University

Two-dimensional (2D) $\text{Cu}_2\text{ZnSnS}_4$ nanosheets were assembled on 2D Bi_2WO_6 nanosheets to efficiently facilitate the separation and transfer of the photogenerated charges for the photo-Fenton degradation of TC-HCl.

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具有可见光增强芬顿活性的II型2D/2D $\text{Cu}_2\text{ZnSnS}_4/\text{Bi}_2\text{WO}_6$ 异质结

郭 莉, 张开来, 韩宣宣, 赵 强, 张媛媛, 戚 勉, 王丹军*, 付 峰#

延安大学化学与化工学院, 陕西省化学反应工程重点实验室, 陕西延安716000

摘要: 高级氧化工艺(AOPs)是一种处理有机污染物的极具吸引力的技术. 大量的前期研究工作集中在通过芬顿反应(Fenton)降解有机污染物. 然而, 芬顿反应需要在酸性条件下进行, 必须在其过程中进行预处理. 同时, 反应后产生的含铁污泥需要进一步处理以满足排放要求, 从而限制了芬顿反应的发展. 作为另一种AOPs, 光催化技术因反应条件温和、操作简单和选择性好等优点受到广泛关注. 研究表明, 各种铁基和铜半导体光催化材料形成光-芬顿(Photo-Fenton)系统, 可有效解决芬顿反应中高价金属离子/低价金属离子的循环问题. 为了充分利用芬顿氧化技术和光催化氧化技术在降解有机污染物方面的各自优势, 构建具有宽太阳光谱响应的新型光芬顿催化剂具有重要意义.

由于其独特的层状结构和优越的有机光催化性能, Bi_2WO_6 作为结构最为简单的钙钛矿型层状氧化物, 其禁带宽度为2.6–2.8 eV, 可响应可见光, 已成研究最多的光催化材料之一. 研究表明, 将 Bi_2WO_6 与合适的助催化剂耦合以构建异质结是提高光生载流子分离效率、拓宽 Bi_2WO_6 可见光响应范围的一种有效策略. 在众多的窄带隙半导体助催化材料中, $\text{Cu}_2\text{ZnSnS}_4$ 作为一种p-型窄带隙半导体, 可以响应可见光甚至近红外光. 近年来, 已经广泛报道了 $\text{Cu}_2\text{ZnSnS}_4$ 可以作为与其他半导体光催化剂进行结合以提高光催化活性的有效助催化剂.

在本文中, 新型 $\text{Cu}_2\text{ZnSnS}_4/\text{Bi}_2\text{WO}_6$ (CZTS/BWO)异质结构通过简单的二次溶剂热法构建. 异质结的成功形成得到了一系列表征方法的证实, 比如XPS和HR-TEM. 光催化活性结果表明, 制备的CZTS/BWO异质结对有机污染物的降解具有优异的光催化性能, 特别是当CZTS相对于异质结中BWO的质量分数为2%时. 此外, 加入过氧化氢(H_2O_2)可进一步提高染料和抗生素的降解效率. 增强的光催化和光芬顿降解性能主要是由于BWO的引入, 其提供了更多的活性位点, 扩展了太阳光谱响应范围并加速了 $\text{Cu(II)}/\text{Cu(I)}$ 的循环. 催化剂的催化活性在经过四次循环实验后并没有显著降低. 最终我们合理假设了光催化和光-芬顿催化机理. 本研究可为设计新型光-芬顿催化剂提供新的视角, 即共同利用光催化活性和芬顿活性进行废水中残留有机物的净化.

关键词: $\text{Cu}_2\text{ZnSnS}_4$, Bi_2WO_6 , 2D/2D异质结, 光芬顿; 光催化

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*通讯联系人. 电话: (0911)2332037; 传真: (0911)2332037; 电子信箱: wangdj761118@163.com

#通讯联系人. 电话: (0911)2332003; 传真: (0911)2332037; 电子信箱: yadxufeng@126.com

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