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Design of a novel direct Z-scheme BiOIO<sub>3</sub> /Bi<sub>2</sub>WO<sub>6</sub> heterojunction for enhanced photocatalytic degradation of norfloxacin under visible light.

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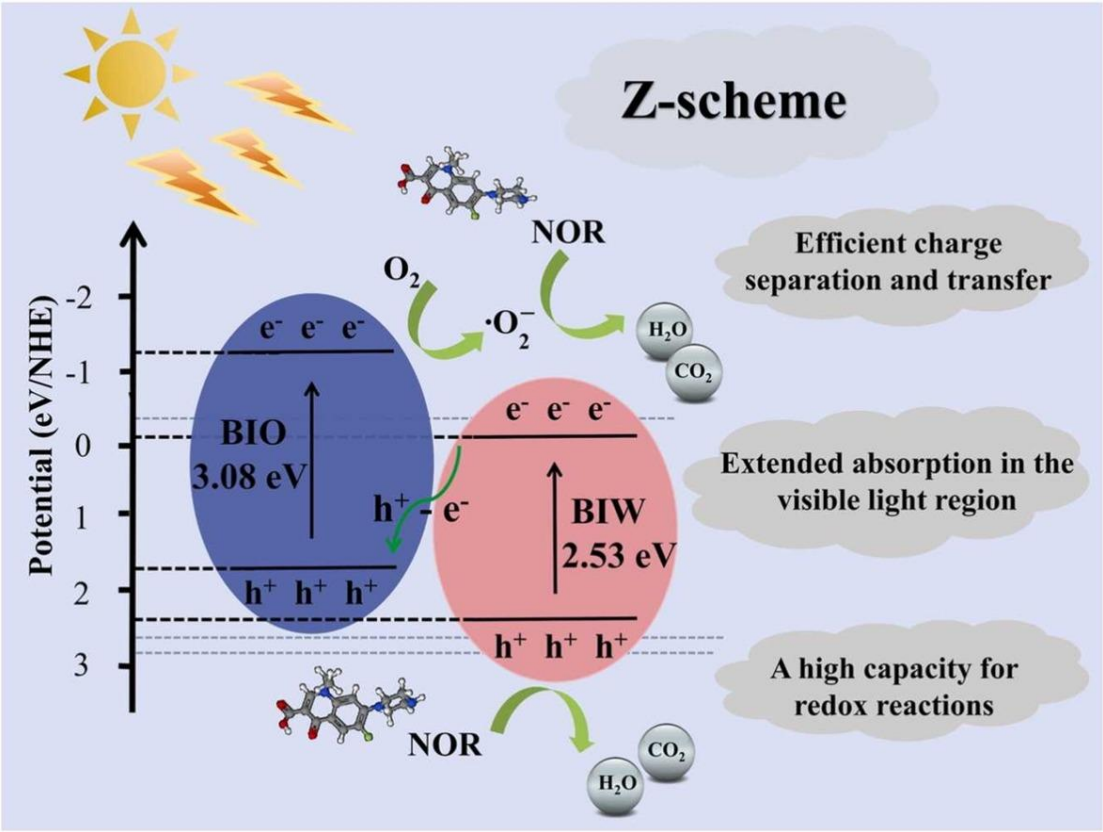
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## Abstract

The unique electronic structure, appropriate bandgap energy, and excellent electron transfer capability make bismuth-based semiconductors hotspots in the field of photocatalysis. Novel BiOIO<sub>3</sub>/Bi<sub>2</sub>WO<sub>6</sub> Z-scheme heterojunctions were fabricated via in-situ hydrothermal synthesis. The BIOBIW-3 heterojunctions (BiOIO<sub>3</sub>:Bi<sub>2</sub>WO<sub>6</sub>=0.25:0.8, mole ratio) exhibited excellent photocatalytic activity for norfloxacin (NOR), with a degradation efficiency of 90.41 % after 90 min of photoreaction and a reaction kinetic constant of 0.02132 min<sup>-1</sup>, which was 5.02 and 9.35 times higher than that of BIO and BIW, respectively. The superior photocatalytic performance can be attributed to the intimate interface between BiOIO<sub>3</sub> and Bi<sub>2</sub>WO<sub>6</sub>, as well as the staggered energy band structure that facilitates the formation of a Z-type heterojunction. This not only widens the range of visible light absorption but also enhances the separation and transfer of photogenerated carriers while maintaining a high capacity for redox reactions. The dominant active species in the degradation process were photogenerated holes (h<sup>+</sup>) and superoxide (·O<sub>2</sub><sup>-</sup>) radicals, and an in-depth exploration of the possible mechanism was conducted. Furthermore, the effects of various parameters, including solution pH, catalyst dosage, and NOR concentration on the photocatalytic degradation of NOR were also investigated. The prepared BiOIO<sub>3</sub>/Bi<sub>2</sub>WO<sub>6</sub> heterojunctions exhibited remarkable photocatalytic performance and chemical stability, presenting a novel research direction for employing layered bismuth-based materials in the degradation of fluoroquinolone antibiotic wastewater.

51     **Graphical Abstract**



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55     **Keywords:** Direct Z-scheme heterojunction; BiOIO<sub>3</sub>/Bi<sub>2</sub>WO<sub>6</sub>; Visible-light photocatalysis;

56     Quinolone antibiotic antibiotics.

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## 1. Introduction

Norfloxacin (NOR), a quinolone antibiotic, has been widely used in the medical field, stockbreeding and aquaculture application[1, 2] due to its advantages including a wide treatment range, low toxicity, and good oral absorption[3]. As one of the most extensively consumed antibiotics globally, NOR has a utilization rate of approximately 30-70% in organisms[4], resulting in the discharge of a significant amount of unused antibiotics into surface and groundwater. Due to its highly mutagenic, teratogenic, and embryotoxic properties, even minute traces of NOR residues and derivatives have the potential to cause eutrophication in ecosystems and contaminate sources of food and drinking water[5]. The persistent chemical properties of NOR hinder its effective removal or degradation through conventional sewage treatment methods[6, 7], leading to the significant accumulation of NOR in the environment. The chronic release of low concentrations of antibiotics into aquatic ecosystems can induce heightened resistance in susceptible bacteria, thereby facilitating the emergence of novel pollutants such as antibiotic resistance genes (ARGs) and antibiotic-resistant bacteria (ARBs)[8-10]. Thus, it is urgent to develop effective treatment methods to remove NOR from the environment.

The removal of norfloxacin from aqueous solutions has been extensively researched, including physical, chemical, biological, and oxidation processes[6, 11]. Advanced oxidation processes (AOPs) are considered an innovative technology for water treatment, possessing inherent characteristics such as environmental friendliness, economic feasibility, and simplicity of implementation[12]. It can degrade NOR into small molecules with high mineralization, which is an environmentally friendly and sustainable way to remove pollutants and has gained considerable popularity. The application of semiconductor photocatalysts, as an effective strategy for environmental purification and energy conversion, has garnered significant attention due to its potential for environmental treatment. Conventional semiconductor materials, including  $\text{TiO}_2$ [13],  $\text{ZnO}$ [14],  $\text{SnO}_2$ [15], and  $\text{WO}_3$ [16], have a wide band gap that results in a high rate of recombination of charge carriers. This phenomenon causes the dissipation of recombined photogenerated electron-hole pairs as thermal energy during internal migration or surface reactions of the semiconductor[17], leading to a decrease in photocatalytic efficiency. Consequently, the development of a novel

photocatalyst with exceptional photocatalytic properties is considered imperative.

Bismuth-based materials exhibit great potential as semiconductor photocatalysts due to the cost-effectiveness, exceptional physicochemical properties, unique layered structure, and favorable energy band structure, and have been widely used [18-20]. Some Bi-based layered photocatalysts such as  $\text{Bi}_2\text{WO}_6$  [21],  $\text{BiOX}$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{F}$ ) [22], and  $\text{BiVO}_4$  [23] have been widely used for pollutant degradation.

$\text{BiOIO}_3$  has been identified as a promising photocatalyst because of its unique photoelectric properties and excellent photocatalytic performance [24], which possesses a layered structure composed of  $(\text{Bi}_2\text{O}_2)^{2+}$  layers of the Aurivillius type interspersed with polar  $(\text{IO}_3)^-$  units [25]. The distinctive 2D-layered structure and non-centrosymmetric crystal arrangement of  $\text{BiOIO}_3$  lead to the creation of an internal polarized electric field, which provides an advantage for the separation of photoexcited charges [26]. Due to its wide bandgap,  $\text{BiOIO}_3$  can only be activated by ultraviolet (UV) light, which limits its practical application as a photocatalyst since UV light accounts for less than 5% of the solar spectrum [27]. To be considered an ideal photocatalyst, a semiconductor material should possess a relatively narrow band gap, along with a negative conduction band bottom and a positive valence band top [28]. To enhance the light absorption range and prevent electron-hole pair recombination, it is advantageous to construct a heterojunction by combining  $\text{BiOIO}_3$ , which is responsive to UV light, with a semiconductor that has a narrower bandgap.

$\text{Bi}_2\text{WO}_6$  is another suitable support with a unique morphology and relatively narrow bandgap energy ( $\sim 2.8$  eV). It is highly regarded for its ability to respond to a wide spectrum of light (around 470 nm) and its characteristic of not causing secondary contamination after use. The structure of  $\text{Bi}_2\text{WO}_6$  is composed of perovskite-like  $[\text{WO}_4]^{2-}$  layers sandwiched between  $[\text{Bi}_2\text{O}_2]^{2+}$  layers. Similar to  $\text{BiOIO}_3$ , this layered structure generates an internal electric field [29], which promotes the separation of electron-hole pairs and thus enhances the photocatalytic performance. The valence band (VB) of  $\text{Bi}_2\text{WO}_6$  emerges from the hybridization of O 2p and Bi 6p orbitals, leading to a broad dispersion of VB, which boosts the movement of electron-hole pairs and improved oxidizing capacity [30].

Herein, we designed and constructed a novel direct Z-scheme heterojunction BiOIO<sub>3</sub>/Bi<sub>2</sub>WO<sub>6</sub> via a facile in-situ growth method for the photocatalytic degradation of NOR. Moreover, the degradation stability and detailed mechanism were also studied to provide further insights into the degradation performance in practical applications.

## 2. Methods

### 2.1 Preparation of BiOIO<sub>3</sub> and Bi<sub>2</sub>WO<sub>6</sub>

The ultrathin BiOIO<sub>3</sub> nanosheets were prepared via a simple hydrothermal method according to previous research[31]. Firstly, 0.485g Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O were dissolved in 80 mL deionized water for 30 min using ultra-sonication, then 0.214 g of KIO<sub>3</sub> was added into the above aqueous solution and stirred continuously for 30 min. Secondly, the mixtures were filled into 150 mL Teflon-lined steel autoclave and reacted at 150 °C for 5 h, then rinsed with water and ethanol through centrifugation after chilling. Eventually, the ultrathin BiOIO<sub>3</sub> nanosheets were dried at 60°C for use and labeled as BIO.

The hydrothermal method was utilized for the synthesis of Bi<sub>2</sub>WO<sub>6</sub> as well[32]. Namely, 0.97g Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O were dissolved in 80 mL deionized water, then 0.05g cetyltrimethylammonium bromide (CTAB) and 0.33g Na<sub>2</sub>WO<sub>4</sub>·2H<sub>2</sub>O was added into the above aqueous solution and stirred continuously for 30 min. Afterwards, the mixtures were filled into a 150 mL Teflon-lined steel autoclave and reacted at 120 °C for 24 h. Subsequent operations are the same. The synthesized Bi<sub>2</sub>WO<sub>6</sub> is named BIW.

### 2.2 Preparation of BiOIO<sub>3</sub>/Bi<sub>2</sub>WO<sub>6</sub> heterojunctions

The BiOIO<sub>3</sub>/Bi<sub>2</sub>WO<sub>6</sub> heterojunctions were synthesized via an in-situ hydrothermal method. 0.25 mol of as-prepared BIO was suspended in 80 mL of deionized water for 30 min using ultrasonication. Then different contents of Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O, CTAB, Na<sub>2</sub>WO<sub>4</sub>·2H<sub>2</sub>O were dispersed into mixtures

illustrated above and stirred continuously for 30 min. Subsequently, the mixed solution was transferred into a 150 mL Teflon-lined autoclave and heated at 120 °C for 24 h. Subsequent operations are the same. Different composites were obtained by varying the molar mass of Bi<sub>2</sub>WO<sub>6</sub> (0.2 mol, 0.4 mol, 0.6 mol 0.8 mol, 0.9 mol), denoting them as BIOBIW-1, BIOBIW-2, BIOBIW-3, BIOBIW-4 respectively.

### *2.3 Photocatalytic experiment*

The photocatalytic activities of as-prepared samples were evaluated for the removal of NOR from aqueous solutions when exposed to visible light. In the degradation experiment, 30 mg of the prepared catalyst was dispersed in 50 ml of NOR solution (10 mg/L). The solution was first stirred in the dark for 30 min to achieve equilibrium between adsorption and desorption. A xenon lamp was then used as the light source and the solution was stirred for 90 min under light conditions. Samples were taken at 15 min intervals and the catalytic activity was assessed by measuring the characteristic peak absorption intensity using a UV-Vis spectrophotometer. The characteristic peak for NOR was at 272.0 nm.

## **3. Results and discussion**

### *3.1 Morphology and structure characterizations*

X-ray diffraction (XRD) analysis was performed to characterize the crystal phase and purity of as-prepared pure BIO, BIW and BIOBIW-x heterojunctions, and the results were shown in Fig. 1a. The (121) plane of BIO exhibits the highest characteristic peaks at 2θ of 27.39°, while the rest of the peaks can be fully attributed to orthorhombic BiOIO<sub>3</sub> based on the ICSD # 262019[33]. For pure BIW, the characteristic peaks at 2θ of 28.43, 33.03, 47.02, and 56.02° are assigned to the (131),

(200), (202), (331) crystal planes of the orthorhombic phase  $\text{Bi}_2\text{WO}_6$  (JCPDS#39-0256)[34]. The characteristic peaks of BIO (121) crystal plane and all the peaks of BIW were observed in BIOBIW-x heterojunctions, indicating the successful synthesis of BIO and BIW. The absence of other characteristic peaks corresponding to different crystal planes of BIO in BIO-BIW heterojunctions is attributed to the strong characteristic peaks of BIW attribution (121) and (331) crystal planes, which effectively shelter them. Furthermore, an increase in BIW content leads to a decrease in the characteristic peak intensity of BIO (121) crystal plane. Hence, a heterostructure consisting of BIO and BIW was created to enhance charge transfer.

FTIR was performed on the BIO, BIW, and BIOBIW-3 heterojunctions (Fig. 1b) to understand the chemical bond vibration. For all catalysts, the absorptive peaks at  $1638$  and  $3430\text{ cm}^{-1}$  are related to the H-O-H and O-H. stretching vibration of the adsorbed  $\text{H}_2\text{O}$  molecule[35, 36]. These adsorbed water molecules play an important role in photocatalytic activity by preventing electron-hole recombination and improving removal efficiency and oxidative elimination of contaminants[37]. The two strong bands can be observed at  $683$  and  $771\text{ cm}^{-1}$ , corresponding to I-O bond vibration of BIO[38]. And the peak at  $517\text{ cm}^{-1}$  is ascribed to the Bi-O stretching vibrations[39]. For pure  $\text{Bi}_2\text{WO}_6$ , the characteristic bands at  $597$ ,  $720$ , and  $1389\text{ cm}^{-1}$  are attributed to the stretching vibrations mode of W-O, Bi-O, and W-O-W, respectively[40]. The W-O, Bi-O, and W-O-W bands attached to BIW is observed in BIOBIW-3 heterojunctions. Nonetheless, the low content of BIO poses a challenge in distinguishing the peaks related to BIO in BIOBIW-3 heterojunctions[41].

The microstructure of BIO, BIW, and BIOBIW-3 heterojunctions was determined from scanning electron microscope (SEM) and transmission electron microscope (TEM) images. The SEM image of BIO in Fig. 2(a) illustrates a structure of relatively smooth amorphous two-dimensional nanosheet with irregular size distribution, which in accordance with the previous reports[39]. The SEM images presented in Fig. 2. (b) reveal that the BIW prepared consists of microrods that are coated with small nanosheets. BIOBIW-3 showed a three-dimensional lamellar flower-like self-assembled structure (Fig. 2c-d) different from that of pure BIO and BIW, suggesting that the introduction of BIW changed the fundamental microstructure of BIO. The TEM micrograph in Fig. 2e-f provides further details on the surface morphology of BIOBIW-3, revealing the intimate interfacial contact between

BIO nanosheets and BIW nanorods. The lattice spacings of 0.323 nm and 0.315 nm can be attributed to the (121) plane of orthorhombic phase  $\text{BiOIO}_3$  (ICSD PDF #262019)[33] and the (131) plane of orthorhombic phase  $\text{Bi}_2\text{WO}_6$  (JCPDS PDF #39-0256)[34, 39], respectively, which is consistent with XRD results. In addition, the energy-dispersive spectroscopy (EDS) (Fig. S1 ) analysis further confirms that BIOBIW-3 contains only Bi, O, I, and W elements, and the atomic percentages of which are consistent with theoretical calculations. The above results prove that the BIOBIW-3 heterojunctions has been successfully synthesized.

The X-ray photoelectron spectroscopy (XPS) profiles of BIO, BIW, and BIOBIW-3 photocatalysts are presented in Fig. 3. The survey profiles in Fig. S2 disclose the specific sample components, Bi, O, I, W, and C elements are observed in BIOBIW-3, the presence of carbon is because of the exotic carbon during the instrumental testing. This is consistent with the EDS results above, further disclosing the composite of BIO and BIW. High-resolution XPS spectra were presented in Fig. 3b-e. In the high-resolution spectra of Bi 4f (Fig. 3a), two detached signal peaks of BIOBIW-3 at 159.24 and 164.54 eV are assigned to Bi  $4f_{7/2}$  and Bi  $4f_{5/2}$  of the  $\text{Bi}^{3+}$  ions in the  $[\text{Bi}_2\text{O}_2]^{2+}$ [42, 43], respectively. The position of the outgoing peaks of BIOBIW-3 is shifted toward higher binding energies relative to BIO and BIW, which implies the formation of surface bismuth defects[44]. In Fig. 3b the O1s peak of BIO and BIW show the characteristic peaks of lattice oxygen at 529.60 and 529.94 eV[45], respectively. Compared to BIO and BIW, the O1s peak of BIOBIW-3 exhibits characteristic peaks of lattice oxygen at higher energy levels, with shifts of 0.46 and 0.12 eV, respectively. The characteristic peaks observed at 531.80 eV, 531.07 eV, and 530.89 eV in BIO, BIW, and BIOBIW-3, respectively, are attributed to the hydroxyl groups bound to water on the surface of the sample[46]. In the I 3d resolution spectra (Fig. 3c), it is observed that the binding energy of pure BIO at 634.90 and 623.40 eV, corresponding to I  $3d_{3/2}$  and I  $3d_{5/2}$  of  $\text{I}^{5+}$ [47], respectively, experiences a negative shift to 630.50 and 619.03 eV in BIOBIW-3 of I<sup>-</sup>. This shift can be attributed to the reduce of  $\text{I}^{5+}$  from  $\text{IO}_3^-$  to  $\text{I}^-$ [48]. In Fig. 3d, the W  $4f_{7/2}$  and W  $4f_{5/2}$  peaks locate at 35.24 eV and 37.38 eV for pure BWO respectively, indicating the  $\text{W}^{6+}$  in the  $[\text{WO}_4]^{2-}$ [49]. While for BIOBIW-3 heterojunctions, the binding energies of W 4f were slight red shift to 35.48 and 37.62 eV, respectively, which could be indexed to the synergistic effect of BIO and BWO[50]. The BIOBIW-3 heterojunctions exhibited slight changes in the Bi 4f, O1s, I 3d, and W 4f peaks

compared to BIO and BIW. Specifically, the binding energy of the Bi and W 4f state in BIOBIW-3 shifted to a higher value compare to BIW, indicating a decrease in electron density on BIW within the BIOBWO-3 structure. On the other hand, the binding energy of the I 3d state in BIOBIW-3 shifted to a lower value, suggesting an increase in electron density on BIO. The observed phenomenon was attributed to electron transfer from BIW to BIO, thus providing evidence of a direct Z-scheme charge transfer pathway between BIO and BIW[51, 52].

### *3.2 Optical properties*

The optical absorption characteristics of the photocatalysts play a significant role in the photocatalytic process. Hence, the optical property of BIO, BIW and BIOBIW-3 heterojunctions were conducted by UV–vis diffuse reflectance spectroscopy (DRS), as shown in Fig. 4a. BIO exhibits a well-established absorption edge at around 398 nm, indicating its exclusive response to UV light. The light absorption band edges of BIW are approximately 430 nm, which proves that it can be excited by visible light. Compared to BIO and BIW, the visible light absorbance of the BIOBIW-3 heterojunctions was found to be further extended, with an absorption edge of 475 nm and a significant increase in absorption intensity in the range of 350-475 nm. It implies that the incorporation of BIW in the BIOBIW-3 heterojunctions makes the absorption edge shift to longer wavelength, which can absorb more light and produce more electrons and holes[48].

Besides excellent optical property, the separation, recombination and migration of photogenerated carriers in catalysts are important for the enhancement of photocatalytic performance. Therefore, the photoelectric chemical properties of BIO, BIW, and BIOBIW-3 heterojunctions were characterized by photoluminescence (PL) spectra, electrochemical impedance spectroscopy (EIS) and transient photocurrent response. For PL, higher ability to separate electrons and holes is associated with weaker and lower peaks, while poorer charge separation ability is indicated by stronger and higher peaks[53]. As shown in Fig. 4b, the photoluminescence intensity of BIOBIW-3 heterojunctions is significantly weaker than that of BIO and BIW, which implies that the

heterojunction formed between BIO and BIW greatly hinders the recombination of photogenerated carriers. The interfacial charge transfer resistance was evaluated by EIS, which showed a smaller semicircular arc in the EIS Nyquist plots, indicating a weaker in charge transfer resistance[54, 55]. Fig. 4c shows that BIOBIW-3 has a smaller radius than BIO and BIW, indicating its lowest charge transfer resistance as well as superior interfacial charge transfer capacity. According to the Fig. 4d, BIOBIW-3 heterojunctions has the highest transient photocurrent density, which is 1.78 and 2.70 times higher than that of BIO and BIW, respectively, further suggesting a faster charge transfer capability[55]. The above results show that BIOBIW-3 heterojunctions have excellent photoelectrochemical properties. The heterojunction formed between BIO and BIW enhances charge separation and reduces electron transfer resistance, so that the photogenerated carriers are easily transferred to the surface of the reactants[40, 53], which greatly improves the photocatalytic performance.

### 3.3 Photocatalytic performance

#### 3.3.1 Photocatalytic performance of NOR degradation

The photocatalytic performance of BIO, BIW, and BIOBIW-x heterojunctions were evaluated for NOR degradation under visible light irradiation. According to Fig. 5a, BIO and BIW exhibited low catalytic behavior, degrading only 40.8% and 24.6% of NOR within 90 min, respectively, while the BIOBIW-x heterojunctions displayed significant photocatalytic activity. And the BIOBIW-x heterojunctions had the highest NOR photodegradation efficiency of 90.41% (82.85% for BIOBIW-1, 88.89% for BIOBIW-2, and 72.91% for BIOBIW-4). However, the photoactivity of BIOBIW-4 composites decreases with excessive BIW, which weaks light trapping and serves as a recombination center for photogenerated carriers, thus reducing their separation efficiency[56, 57]. The NOR degradation data were fitted with the first-order kinetics model as follows[42]:  $\ln(C_0/C)=kt$ , where  $k$ ,  $C_0$ , and  $C$  are the reaction kinetic constant, the NOR concentration at the radiation time of 0 and  $t$ , respectively. Fig 5b demonstrated that BIOBIW-3 heterojunctions reached maximum  $k$  of  $0.02132 \text{ min}^{-1}$ , which was 5.02 and 9.35 times higher than BIO and BIW,

respectively. Therefore, the formation of heterojunctions between BIO and BIW leads to a significant increase in NOR degradation efficiency.

Probing the recyclability and stability of prepared BIOBIW-3 composites is crucial for practical applications. As shown in Figure 5c, the NOR photodegradation efficiency was still more than 70% after four recycles (decreased from 89.14% to 72.74%), which was attributed to the unavoidable loss of catalyst during the recovery procedure[58]. Moreover, the FTIR spectra analysis revealed that the chemical bonding vibrations of BIOBIW-3 remained consistent before and after the reaction (Fig. 5d), indicating that the photocatalyst has high structural stability.

### 3.3.2 Factors affecting NOR degradation

Considering the complexity of environmental pollution, a comprehensive study of the effects of solution pH, catalyst dosage, and NOR concentration is necessary for the photocatalytic degradation of NOR by BIOBIW-3 heterojunctions (Fig. S3a-c). The photocatalytic process is significantly influenced by the solution pH, which affects various aspects such as the surface charge of the photocatalyst, nanoparticle aggregation, and the energy band potential[59]. In Fig S3(a), the NOR degradation efficiency exhibited a notable increase from 40.04% to 94.87% as the pH rose from 3 to 9. However, with a further increase in pH to 11, the NOR degradation efficiency decreased to 80.62%. Obviously, BIOBIW-3 exhibits excellent performance under neutral or alkaline conditions. This may be due to the fact that the solution pH increases and the concentration of  $H^+$  decreases correspondingly, resulting in fewer  $\cdot O_2^-$  reacting with  $H^+$ . Therefore, more  $\cdot O_2^-$  can participate in the photocatalytic degradation of NOR[60], which is the dominant reactive oxygen species for photocatalytic degradation of NOR.

It is imperative to identify a catalyst concentration that strikes a balance between cost-effectiveness and efficiency. As shown in Fig S3(b), the degradation efficiency of NOR increased from 80.96% to 86.52% with the increase of catalyst dosage from 0.4 g/L to 0.6 g/L. By increasing the amount of catalysts, the number of active sites and free radicals can be increased, resulting in a faster reaction rate[59]. However, the high degradation efficiency at dosages above 0.7 g/L was due to the fact that

more than half of the NOR was adsorbed[34].

The impact of varying initial concentrations (ranging from 5 to 20 mg/L) on the photoactivity was investigated, as depicted in Fig S3(c). The degradation efficiency exceeds 90% for the initial concentrations of NOR at 10mg/L and 15mg/L, but decreases to 82.74% when the concentration of NOR reaches 20mg/L. This could be attributed to the higher NOR concentration, which not only competes with the catalyst for the absorption of photons, but also increases the adsorption of NOR molecules on the surface of the catalyst, covering the active sites[58, 61].

#### *3.4 Photocatalytic mechanism of BIOBIW-3 heterojunctions*

The photogenerated carriers by photoexcitation react with oxygen ( $O_2$ ), water ( $H_2O$ ), and hydroxyl groups, leading to the production of reactive oxygen species (ROS) including hydroxyl radicals ( $\cdot OH$ ) and superoxide radical anions ( $\cdot O_2^-$ )[62]. The degradation and mineralization of organic pollutants in wastewater depend on these ROS[63]. Capture experiments were conducted to investigate the activity species involved in the photodegradation of NOR by BIOBIW-3, using BQ (0.1 mmol/L), IPA (100 mmol/L), and FA (100 mmol/L) for capturing hydroxyl holes ( $h^+$ ), radicals ( $\cdot OH$ ), and superoxide radical anions ( $\cdot O_2^-$ ), respectively. As depicted in Fig. 6a, the NOR degradation efficiency barely decreased after the addition of IPA, suggesting that  $\cdot OH$  is not the vital active species in the degradation process. However, the introduction of FA and BA had a notable inhibit on the degradation of NOR, resulting in a 52.46% and 26.18% reduction in photocatalytic efficiencies, respectively, compared to no scavenger system. The above results revealed that  $h^+$  play a major role and  $\cdot O_2^-$  play a subordinate role in the photocatalytic mechanism of BIOBIW-3 degradation of NOR. ESR spin-trapping spectra were used to further confirmed the photocatalytic mechanism of BIOBIW (Fig. 6b). After the addition of DMPO (trapping agents), the strong characteristic signal of  $DMPO-\cdot O_2^-$  was detected under visible light irradiation, while the signal of  $DMPO-\cdot OH$  was almost undetectable. These results of ESR spectra are consistent with the capture experiments described above.

The band gap energy ( $E_g$ ) of photocatalysts was determined from the Kubelka-Munk equation as follows[64]:  $\alpha hv = A(hv - E_g)^{n/2}$ , which  $\alpha$ ,  $hv$ , and  $A$  are the absorption coefficient, photon energy, and a constant, respectively. Both of BIO and BIW are indirect transition semiconductor, so for them,  $n$  is 4[35, 65]. The valence band (VB) and conduction band (CB) potentials of the photocatalyst play a crucial role in the redox ability of photogenerated carriers[40]. The valence band energy ( $E_{VB}$ ) of BIO and BIW were further obtained by analyzing the VB-XPS spectrum (Fig. 6c), which were 2.39 eV and 1.80 eV, respectively. The band gap energy of BIO, BIW, and BIOBIW-3 can be estimated from the  $(\alpha hv)^{1/2}$  VS  $hv$  plot (Fig. 6d), which are found to be 3.04 eV, 2.69 and 2.41 eV, respectively. Thus, the conduction band potential ( $E_{CB}$ ) of BIO and BIW was determined to be -1.24 eV and -0.30 eV, respectively, using the following empirical formulas[58]:  $E_{VB} = E_{CB} + E_g$ .

The band gap position of the semiconductor determines the direction of migration and the degree of effective separation of photogenerated electrons and holes[35, 66]. Based on the structural positions of the BIO and BIW energy bands (Fig. 7a), the electron-hole transfer mechanism for the photocatalytic degradation of NOR by BIOBIW-3 was first hypothesized to be conventional type II heterojunction. When irradiated with visible light, the electrons in the VB of BIO and BIW are excited to form electron-hole pairs, and then the electrons are transferred to the CB, with a corresponding number of photogenerated holes remaining in the VB. As both VB and CB energy band positions of BIO are higher than that of BIW, photogenerated electrons flow from BIO to BIW and photogenerated holes flow from BIW to BIO. However, the reduction potential of  $O_2/\cdot O_2^-$  was -0.33 eV [5, while the CB of BIW (-0.28 eV) was not sufficient to reduce  $O_2$  to  $\cdot O_2^-$ , which contradicts the above results of the reactive free radical trapping assay and ESR experiment. Therefore, the traditional type-II heterojunction cannot explain the photocatalytic mechanism of the BIOBIW-3. Considering the previous discussion, the direct Z-scheme NOR photodegradation mechanism of BIOBIW-3 composites is rationally proposed as shown in Fig. 7b. Due to the difference in the work function, an internal electric field from BIO to BIW is formed upon contact between BIO and BIW, which results in the transfer of  $e^-$  on the CB of BIW to BIO and recombination with  $h^+$  on the VB of BIO.

As a result, the strongly reducing photogenerated electrons in the CB of the BIO and the strongly oxidizing holes in the VB of the BIW are retained for photocatalytic degradation of NOR. The more negative  $E_{CB}$  potential of BIO (-1.24 eV) in comparison to the standard redox potential of  $O_2/\cdot O_2^-$  (-0.33 eV) allows for the conversion of  $O_2$  to  $\cdot O_2^-$ . Additionally, the  $E_{VB}$  potential of BIW (2.39 eV) is also negative than the standard redox potentials of  $OH^\cdot/\cdot OH$  (+2.40 eV) and  $H_2O/\cdot OH$  (+2.72 eV)[67, 68], indicating that oxidation of  $h^+$  to  $\cdot OH$  is impossible. Hence  $h^+$  on the CB of BIW are straightforwardly involved in NOR oxidation. The aforementioned results align with band gap analysis, X-ray photoelectron spectroscopy (XPS), electron paramagnetic resonance (EPR) spectroscopy, and radical scavenging assays, confirming that BIOBIW-3 follows the charge transfer mechanism of a Z-type heterojunction. The formation of Z-scheme heterojunction in BIOBIW-3 composite could effectively improve electron-hole pairs separation, expand the range of light responsiveness and retain the high redox potentials of a single semiconductor, which contributed to the higher photocatalytic activity.

## 4. Conclusion

A direct Z-scheme BiOIO<sub>3</sub>/Bi<sub>2</sub>WO<sub>6</sub> heterojunction with interfacial contact was successfully synthesized via in-situ hydrothermal methods for the degradation of NOR. The light absorption range of the BiOIO<sub>3</sub>/Bi<sub>2</sub>WO<sub>6</sub> heterojunction was enhanced by combining UV-light-responsive BiOIO<sub>3</sub> and visible-light-responsive Bi<sub>2</sub>WO<sub>6</sub>. The Z-scheme mechanism formed by BiOIO<sub>3</sub>/Bi<sub>2</sub>WO<sub>6</sub> photocatalyst promotes efficient charge separation and decreases migration resistance, leading to enhanced oxidation-reduction capabilities of the individual photocatalysts, thereby improving overall photocatalytic performance. The heterojunction more efficiently produces  $\cdot\text{O}_2^-$ , a key active radical in NOR photocatalytic oxidation, with holes significantly influencing the reaction process. As a result, BIOBIW-3 heterojunctions exhibited the highest photocatalytic activity, with a 90.41% NOR degradation efficiency for 90 minutes of light reaction. Surprisingly, the crystal structure and photocatalytic activity of the BIOBIW-3 heterojunctions remained largely unchanged even after 5 cycles. In addition, the BIOBIW-3 heterojunctions had the highest degradation rate of NOR at pH = 9, NOR concentration at 10 mg/L, and catalyst concentration at 0.7 g/L. This study provides a facile and feasible method to prepare layered bismuth-based semiconductor heterojunctions to optimize the photocatalytic degradation performance of fluoroquinolone antibiotics.

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## Reference

- [1] Y. Li, Z. Wang, X. Xie, J. Zhu, R. Li, T.J.C. Qin, S.A. Physicochemical, E. Aspects, Removal of Norfloxacin from aqueous solution by clay-biochar composite prepared from potato stem and natural attapulgite, 514 (2017) 126-136.
- [2] S.A. Hussain, S.O. Prasher, R.M.J.E.e. Patel, Removal of ionophoric antibiotics in free water surface constructed wetlands, 41 (2012) 13-21.
- [3] Z. Wang, B. Song, J. Li, X.J.C. Teng, Degradation of norfloxacin wastewater using kaolin/steel slag particle electrodes: Performance, mechanism and pathway, 270 (2021) 128652.
- [4] Z. Chu, T. Chen, H. Liu, D. Chen, X. Zou, H. Wang, F. Sun, P. Zhai, M. Xia, M.J.C. Liu, Degradation of norfloxacin by calcite activating peroxymonosulfate: performance and mechanism, 282 (2021) 131091.
- [5] B. Ji, W. Zhao, J. Duan, L. Fu, L. Ma, Z.J.R.a. Yang, Immobilized  $\text{Ag}_3\text{PO}_4/\text{GO}$  on 3D nickel foam and its photocatalytic degradation of norfloxacin antibiotic under visible light, 10 (2020) 4427-4435.
- [6] L. Zhang, Y. Meng, T. Dai, Y. Yao, H. Shen, B. Xie, Z. Ni, S.J.A.C.S. Xia, Fabrication of a coated  $\text{BiVO}_4@$  LDHs Z-scheme heterojunction and photocatalytic degradation of norfloxacin, 219 (2022) 106435.
- [7] Z. Lu, Z. Yu, J. Dong, M. Song, Y. Liu, X. Liu, Z. Ma, H. Su, Y. Yan, P.J.C.E.J. Huo, Facile microwave synthesis of a Z-scheme imprinted  $\text{ZnFe}_2\text{O}_4/\text{Ag}/\text{PEDOT}$  with the specific recognition ability towards improving photocatalytic activity and selectivity for tetracycline, 337 (2018) 228-241.
- [8] A. Ahtesham, M. Shahadat, E. Hussain, R. Adnan, S.Z. Ahammad, R. Jain, K.J.J.o.W.P.E. Raees, Treatment of antibiotic-resistant genes via photocatalytic-assisted Microbial Fuel Cells: A review, 55 (2023) 104126.
- [9] H. Zhou, J. Cui, L. Pang, Y. Wangjin, M. Li, Z. Zhao, L.J.J.o.C.P. Huang, Removal of antibiotics and antibiotic resistance genes from urban rivers using a photocatalytic-and-bionic artificial ecosystem, 348 (2022) 131311.
- [10] M.-T. Guo, Q.-B. Yuan, J.J.C. Yang, Ultraviolet reduction of erythromycin and tetracycline resistant heterotrophic bacteria and their resistance genes in municipal wastewater, 93 (2013)

2864-2868.

- [11] M. Sayed, L.A. Shah, J.A. Khan, N.S. Shah, J. Nisar, H.M. Khan, P. Zhang, A.R.J.T.J.o.P.C.A. Khan, Efficient photocatalytic degradation of norfloxacin in aqueous media by hydrothermally synthesized immobilized  $\text{TiO}_2/\text{Ti}$  films with exposed  $\{001\}$  facets, 120 (2016) 9916-9931.
- [12] M.F.R. Samsudin, S. Sufian, B.J.J.o.M.L. Hameed, Epigrammatic progress and perspective on the photocatalytic properties of  $\text{BiVO}_4$ -based photocatalyst in photocatalytic water treatment technology: A review, 268 (2018) 438-459.
- [13] L. Baia, E. Orbán, S. Fodor, B. Hampel, E.Z. Kedves, I. Székely, É. Karácsnyi, B. Réti, P. Berki, A.J.M.S.i.S.P. Vulpoi, Preparation of  $\text{TiO}_2/\text{WO}_3$  composite photocatalysts by the adjustment of the semiconductors' surface charge, 42 (2016) 66-71.
- [14] G. Yang, W. Yan, Q. Zhang, S. Shen, S.J.N. Ding, One-dimensional  $\text{CdS}/\text{ZnO}$  core/shell nanofibers via single-spinneret electrospinning: tunable morphology and efficient photocatalytic hydrogen production, 5 (2013) 12432-12439.
- [15] M. Aslam, M.T. Qamar, S. Ali, A.U. Rehman, M. Soomro, I. Ahmed, I. Ismail, A.J.J.o.e.m. Hameed, Evaluation of  $\text{SnO}_2$  for sunlight photocatalytic decontamination of water, 217 (2018) 805-814.
- [16] M. Reli, L. Svoboda, M. Šíhor, I. Troppová, J. Pavlovský, P. Praus, K.J.E.S. Kočí, P. Research, Photocatalytic decomposition of  $\text{N}_2\text{O}$  over  $\text{g-C}_3\text{N}_4/\text{WO}_3$  photocatalysts, 25 (2018) 34839-34850.
- [17] Z. Shayegan, C.-S. Lee, F.J.C.E.J. Haghighat,  $\text{TiO}_2$  photocatalyst for removal of volatile organic compounds in gas phase—A review, 334 (2018) 2408-2439.
- [18] L. Huang, Z. Duan, Y. Song, Q. Li, L.J.A.A.N.M. Chen,  $\text{BiVO}_4$  microplates with oxygen vacancies decorated with metallic Cu and Bi nanoparticles for  $\text{CO}_2$  photoreduction, 4 (2021) 3576-3585.
- [19] K. Xu, L. Wang, X. Xu, S.X. Dou, W. Hao, Y.J.E.S.M. Du, Two dimensional bismuth-based layered materials for energy-related applications, 19 (2019) 446-463.
- [20] R. He, D. Xu, B. Cheng, J. Yu, W.J.N.H. Ho, Review on nanoscale Bi-based photocatalysts, 3 (2018) 464-504.
- [21] J. Hou, S. Cao, Y. Wu, F. Liang, Y. Sun, Z. Lin, L.J.N.E. Sun, Simultaneously efficient light

- absorption and charge transport of phosphate and oxygen-vacancy confined in bismuth tungstate atomic layers triggering robust solar CO<sub>2</sub> reduction, 32 (2017) 359-366.
- [22] S. Qi, X. Liu, N. Ma, H.J.C.P.L. Xu, Construction and photocatalytic properties of WS<sub>2</sub>/MoS<sub>2</sub>/BiOCl heterojunction, 763 (2021) 138203.
- [23] Y. Wang, G. Tan, T. Liu, Y. Su, H. Ren, X. Zhang, A. Xia, L. Lv, Y.J.A.C.B.E. Liu, Photocatalytic properties of the g-C<sub>3</sub>N<sub>4</sub>/ {010} facets BiVO<sub>4</sub> interface Z-Scheme photocatalysts induced by BiVO<sub>4</sub> surface heterojunction, 234 (2018) 37-49.
- [24] D.H. Cui, Y.F. Zheng, X.C.J.J.o.E.N. Song, Hydrothermal synthesis, characterisation and photocatalytic properties of BiOIO<sub>3</sub> nanoplatelets, 11 (2016) 1000-1010.
- [25] W. Wang, B. Huang, X. Ma, Z. Wang, X. Qin, X. Zhang, Y. Dai, M.H.J.C.A.E.J. Whangbo, Efficient separation of photogenerated electron - hole pairs by the combination of a heterolayered structure and internal polar field in pyroelectric BiOIO<sub>3</sub> nanoplates, 19 (2013) 14777-14780.
- [26] C. Zeng, Y. Hu, H.J.A.S.C. Huang, Engineering, BiOBr<sub>0.75</sub>I<sub>0.25</sub>/BiOIO<sub>3</sub> as a novel heterojunctional photocatalyst with superior visible-light-driven photocatalytic activity in removing diverse industrial pollutants, 5 (2017) 3897-3905.
- [27] C. Xu, Y.J.A.B. Wan, Discussion on Preparation and Application of BiOIO<sub>3</sub>-based Composite Materials, 9 (2020) 104-135.
- [28] Z. Saddique, M. Imran, A. Javaid, F. Kanwal, S. Latif, J.C.S. dos Santos, T.H. Kim, G.J.I.J.o.H.E. Boczkaj, Bismuth-based nanomaterials-assisted photocatalytic water splitting for sustainable hydrogen production, (2023).
- [29] A. Elaouni, M. El Ouardi, A. BaQais, M. Arab, M. Saadi, H.A.J.R.a. Ahsaine, Bismuth tungstate Bi<sub>2</sub>WO<sub>6</sub>: a review on structural, photophysical and photocatalytic properties, 13 (2023) 17476-17494.
- [30] H. Yi, L. Qin, D. Huang, G. Zeng, C. Lai, X. Liu, B. Li, H. Wang, C. Zhou, F.J.C.E.J. Huang, Nano-structured bismuth tungstate with controlled morphology: fabrication, modification, environmental application and mechanism insight, 358 (2019) 480-496.
- [31] Z. Ji, J. Wu, F. Tian, Q. Liu, L. Zhao, C. Qu, F. Li, X. Qi, Y. Guan, Y.J.C.L. Zhang, Fabrication of Carbon-Modified BiOI/BiOIO<sub>3</sub> Heterostructures With Oxygen Vacancies for Enhancing Photocatalytic Activity, 148 (2018) 3349-3362.
- [32] X. Chen, Z. Zhu, Y. Zhao, Y. Song, Y.J.S. Bu, Interfaces, Interface engineering for bismuth

tungstate and lanthanum cobaltate towards promoted sulfamethoxazole photocatalytic oxidation,  
38 (2023) 102786.

[33] S. Chu, H.-L. Wang, H. Huang, G.-J. Jiang, R. Yan, W.-F.J.A.S.S. Jiang, Facile synthesis of  
AgIO<sub>3</sub>/BiOIO<sub>3</sub> Z-scheme binary heterojunction with enhanced photocatalytic performance for  
diverse persistent organic pollutants degradation, 588 (2022) 152966.

[34] H. Yin, C. Yuan, H. Lv, K. Zhang, X. Chen, Y. Zhang, Y.J.P.T. Zhang, Fabrication of 2D/1D  
Bi<sub>2</sub>WO<sub>6</sub>/C<sub>3</sub>N<sub>5</sub> heterojunctions for efficient antibiotics removal, 413 (2023) 118083.

[35] L. Kan, C. Chang, Q. Wang, X.J.S. Wang, P. Technology, Glycol assisted splitting BiOIO<sub>3</sub>  
into plasmonic bismuth coupled with BiOI co-modified Bi<sub>2</sub>WO<sub>6</sub> (BiOI/Bi/Bi<sub>2</sub>WO<sub>6</sub>) to form  
indirect Z-scheme heterojunction for efficient photocatalytic degradation of BPA, 297 (2022)  
121537.

[36] J. Chen, Y. Xiao, N. Wang, X. Kang, D. Wang, C. Wang, J. Liu, Y. Jiang, H.J.S.C.M. Fu,  
Facile synthesis of a Z-scheme CeO<sub>2</sub>/C<sub>3</sub>N<sub>4</sub> heterojunction with enhanced charge transfer for CO<sub>2</sub>  
photoreduction, (2023) 1-11.

[37] M. Dai, R. Xue, M. Liu, Z.J.J.o.A. Wang, Compounds, Hydrothermal synthesis of porous  
CdS/Bi<sub>2</sub>S<sub>3</sub>/BiOIO<sub>3</sub> nanocomposites for solar-driven photocatalytic degradation of rhodamine B,  
971 (2024) 172784.

[38] J. Xie, Y. Cao, J. Hu, Y. Tang, D.J.G.C. Jia, A solvent-free strategy to realize the substitution  
of I<sup>-</sup> for IO<sub>3</sub><sup>3-</sup> in a BiOIO<sub>3</sub> photocatalyst with an opposite charge transfer path, 22 (2020) 1424-  
1431.

[39] D.-E. Lee, S. Moru, K.P. Reddy, W.-K. Jo, S.J.J.o.M.S. Tonda, Technology, 2D/2D BiOIO<sub>3</sub>/g-  
C<sub>3</sub>N<sub>4</sub> S-scheme hybrid heterojunction with face-to-face interfacial contact for effective  
photocatalytic H<sub>2</sub> production and norfloxacin degradation, 148 (2023) 19-30.

[40] Y. Jia, X. Zhang, R. Wang, J. Yuan, R. Zheng, J. Zhang, F. Qian, Y. Chen, M. Zhang,  
L.J.A.S.S. Guo, Energy band engineering of WO<sub>3</sub>/Bi<sub>2</sub>WO<sub>6</sub> direct Z-scheme for enhanced  
photocatalytic toluene degradation, 618 (2023) 156636.

[41] Z. Zhu, C. Zhu, R. Yang, L. Yan, C. Hu, B.J.S. Liu, P. Technology, Fabrication of 3D  
Bi<sub>5</sub>O<sub>7</sub>I/BiOIO<sub>3</sub> heterojunction material with enhanced photocatalytic activity towards tetracycline  
antibiotics, 265 (2021) 118522.

[42] J. Guo, L. Wang, X. Wei, Z.A. Alothman, M.D. Albaqami, V. Malgras, Y. Yamauchi, Y. Kang,

- M. Wang, W.J.J.o.H.M. Guan, Direct Z-scheme CuInS<sub>2</sub>/Bi<sub>2</sub>MoO<sub>6</sub> heterostructure for enhanced photocatalytic degradation of tetracycline under visible light, 415 (2021) 125591.
- [43] L. Kan, L. Yang, W. Mu, Q. Wang, X. Wang, C.J.J.o.C. Chang, I. Science, Facile one-step strategy for the formation of BiOIO<sub>3</sub>/[Bi<sub>6</sub>O<sub>6</sub>(OH)<sub>3</sub>](NO<sub>3</sub>)<sub>3</sub>·1.5H<sub>2</sub>O heterojunction to enhancing photocatalytic activity, 612 (2022) 401-412.
- [44] Y. Ling, J. Wu, X. Man, Y. Xu, Q. Liu, Y. Qi, Q. Wu, X. Qi, T. Jia, Z.J.M.R.B. Guo, BiOIO<sub>3</sub>/graphene interfacial heterojunction for enhancing gaseous heavy metal removal, 122 (2020) 110620.
- [45] D.-E. Lee, N. Mamede, K.P. Reddy, B.M. Abraham, W.-K. Jo, S.J.J.o.M.S. Tonda, Technology, Bifunctional S-scheme hybrid heterojunction comprising CdS nanorods and BiOIO<sub>3</sub> nanosheets for efficient solar-induced antibiotic degradation and highly-selective CO<sub>2</sub> reduction, 161 (2023) 74-87.
- [46] L. Kan, W. Mu, C. Chang, F.J.S. Lian, P. Technology, Dual S-scheme graphitic carbon-doped α-Bi<sub>2</sub>O<sub>3</sub>/β-Bi<sub>2</sub>O<sub>3</sub>/Bi<sub>5</sub>O<sub>7</sub>I ternary heterojunction photocatalyst for the degradation of Bisphenol A, 312 (2023) 123388.
- [47] T. Xiong, H. Zhang, Y. Zhang, F.J.C.J.o.C. Dong, Ternary Ag/AgCl/BiOIO<sub>3</sub> composites for enhanced visible-light-driven photocatalysis, 36 (2015) 2155-2163.
- [48] M. Lu, X. Xiao, Y. Wang, J.J.J.o.A. Chen, Compounds, Construction of novel BiOIO<sub>3</sub>/MoS<sub>2</sub> 2D/2D heterostructures with enhanced photocatalytic activity, 831 (2020) 154789.
- [49] C. Yang, H. Chai, P. Xu, P. Wang, X. Wang, T. Shen, Q. Zheng, G.J.S. Zhang, P. Technology, One-step synthesis of a 3D/2D Bi<sub>2</sub>WO<sub>6</sub>/g-C<sub>3</sub>N<sub>4</sub> heterojunction for effective photocatalytic degradation of atrazine: Kinetics, degradation mechanisms and ecotoxicity, 288 (2022) 120609.
- [50] Y. Zhao, X. Fan, H. Zheng, E. Liu, J. Fan, X.J.J.o.M.S. Wang, Technology, Bi<sub>2</sub>WO<sub>6</sub>/AgInS<sub>2</sub> S-scheme heterojunction: efficient photodegradation of organic pollutant and toxicity evaluation, 170 (2024) 200-211.
- [51] W. Yu, D. Xu, T.J.J.o.M.C.A. Peng, Enhanced photocatalytic activity of g-C<sub>3</sub>N<sub>4</sub> for selective CO<sub>2</sub> reduction to CH<sub>3</sub>OH via facile coupling of ZnO: a direct Z-scheme mechanism, 3 (2015) 19936-19947.
- [52] J. Low, B. Dai, T. Tong, C. Jiang, J.J.A.M. Yu, In situ irradiated X - ray photoelectron spectroscopy investigation on a direct Z - scheme TiO<sub>2</sub>/CdS composite film photocatalyst, 31

(2019) 1802981.

[53] Y. Xiao, S. Tan, D. Wang, J. Wu, T. Jia, Q. Liu, Y. Qi, X. Qi, P. He, M.J.A.S.S. Zhou, CeO<sub>2</sub>/BiOIO<sub>3</sub> heterojunction with oxygen vacancies and Ce<sup>4+</sup>/Ce<sup>3+</sup> redox centers synergistically enhanced photocatalytic removal heavy metal, 530 (2020) 147116.

[54] Y. Chen, C. Zhao, S. Ma, P. Xing, X. Hu, Y. Wu, Y.J.I.C.F. He, Fabrication of a Z-scheme AgBr/Bi<sub>4</sub>O<sub>5</sub>Br<sub>2</sub> nanocomposite and its high efficiency in photocatalytic N<sub>2</sub> fixation and dye degradation, 6 (2019) 3083-3092.

[55] M. Lu, X. Xiao, Y. Xiao, J. Li, F.J.J.o.C. Zhang, I. Science, One-pot hydrothermal fabrication of 2D/2D BiOIO<sub>3</sub>/BiOBr Z-scheme heterostructure with enhanced photocatalytic activity, 625 (2022) 664-679.

[56] C. Zhu, Q. He, H. Yao, S. Le, W. Chen, C. Chen, S. Wang, X.J.E.R. Duan, Amino-functionalized NH<sub>2</sub>-MIL-125 (Ti)-decorated hierarchical flowerlike ZnIn<sub>2</sub>S<sub>4</sub> for boosted visible-light photocatalytic degradation, 204 (2022) 112368.

[57] C. Zhu, H. Yao, S. Le, Y. Yin, C. Chen, H. Xu, S. Wang, X.J.C.P.B.E. Duan, S-scheme photocatalysis induced by ultrathin TiO<sub>2</sub> (B) nanosheets-anchored hierarchical In<sub>2</sub>S<sub>3</sub> spheres for boosted photocatalytic activity, 242 (2022) 110082.

[58] D. Peng, Y. Wang, H. Shi, W. Jiang, T. Jin, Z. Jin, Z.J.J.o.C. Chen, I. Science, Fabrication of novel Cu<sub>2</sub>WS<sub>4</sub>/NiTiO<sub>3</sub> heterostructures for efficient visible-light photocatalytic hydrogen evolution and pollutant degradation, 613 (2022) 194-206.

[59] J. Lai, X. Jiang, M. Zhao, S. Cui, J. Yang, Y.J.A.C.B.E. Li, Thickness-dependent layered BiOIO<sub>3</sub> modified with carbon quantum dots for photodegradation of bisphenol A: Mechanism, pathways and DFT calculation, 298 (2021) 120622.

[60] Y. Song, J. Qi, J. Tian, S. Gao, F.J.C.E.J. Cui, Construction of Ag/g-C<sub>3</sub>N<sub>4</sub> photocatalysts with visible-light photocatalytic activity for sulfamethoxazole degradation, 341 (2018) 547-555.

[61] T. Chankhanittha, V. Somaudon, T. Photiwat, S. Youngme, K. Hemavibool, S.J.J.o.P. Nanan, C.o. Solids, Enhanced photocatalytic performance of ZnO/Bi<sub>2</sub>WO<sub>6</sub> heterojunctions toward photodegradation of fluoroquinolone-based antibiotics in wastewater, 153 (2021) 109995.

[62] W.S. Koe, J.W. Lee, W.C. Chong, Y.L. Pang, L.C.J.E.S. Sim, P. Research, An overview of photocatalytic degradation: photocatalysts, mechanisms, and development of photocatalytic membrane, 27 (2020) 2522-2565.

- [63] L. Ai, H. Yin, S. Wang, J. Wang, X. Gao, X. Yin, K. Dou, P. Ju, H.J.M.T.N. Sun, One-pot preparation of Bi/BiOF/Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> Z-scheme heterojunction with enhanced photocatalysis activity for ciprofloxacin degradation under simulated sunlight, (2023) 100446.
- [64] X. Xiao, M. Lu, J. Nan, X. Zuo, W. Zhang, S. Liu, S.J.A.C.B.E. Wang, Rapid microwave synthesis of I-doped Bi<sub>4</sub>O<sub>3</sub>Br<sub>2</sub> with significantly enhanced visible-light photocatalysis for degradation of multiple parabens, 218 (2017) 398-408.
- [65] Y. Qiao, X. Meng, Z.J.A.S.S. Zhang, A new insight into the enhanced visible light-induced photocatalytic activity of NaNbO<sub>3</sub>/Bi<sub>2</sub>WO<sub>6</sub> type-II heterostructure photocatalysts, 470 (2019) 645-657.
- [66] K. Kadeer, Y. Tursun, T. Dilinuer, K. Okitsu, A.J.C.I. Abulizi, Sonochemical preparation and photocatalytic properties of CdS QDs/Bi<sub>2</sub>WO<sub>6</sub> 3D heterojunction, 44 (2018) 13797-13805.
- [67] P. Jing, C. He, S. Huang, H. Li, J. Liu, Y. Cui, Y. Pu, J.J.A.M.T. Wang, 2D Z-scheme heterojunction and oxygen deficiency synergistically boosting the photocatalytic activity of a layered BaTiO<sub>3</sub>/BiOIO<sub>3</sub> composite, 29 (2022) 101574.
- [68] J. Zhang, Z. Zhu, J. Jiang, H.J.M. Li, Synthesis of novel ternary dual Z-scheme AgBr/LaNiO<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub> composite with boosted visible-light photodegradation of norfloxacin, 25 (2020) 3706.

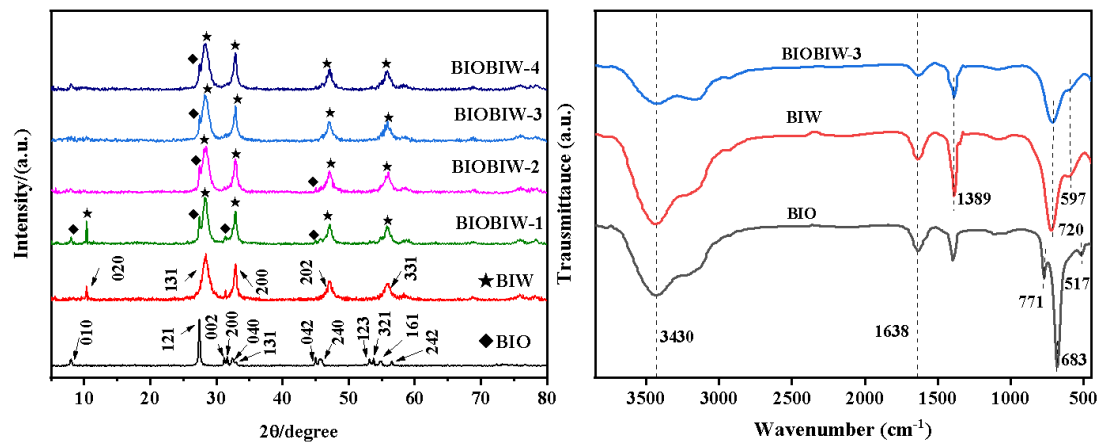


**Fig. 1** (a) XRD spectrum of BIO, BIW, and BIOBIW-x heterojunctions, (b) FTIR spectra of BIO, BIW, and BIOBIW-3 heterojunctions.

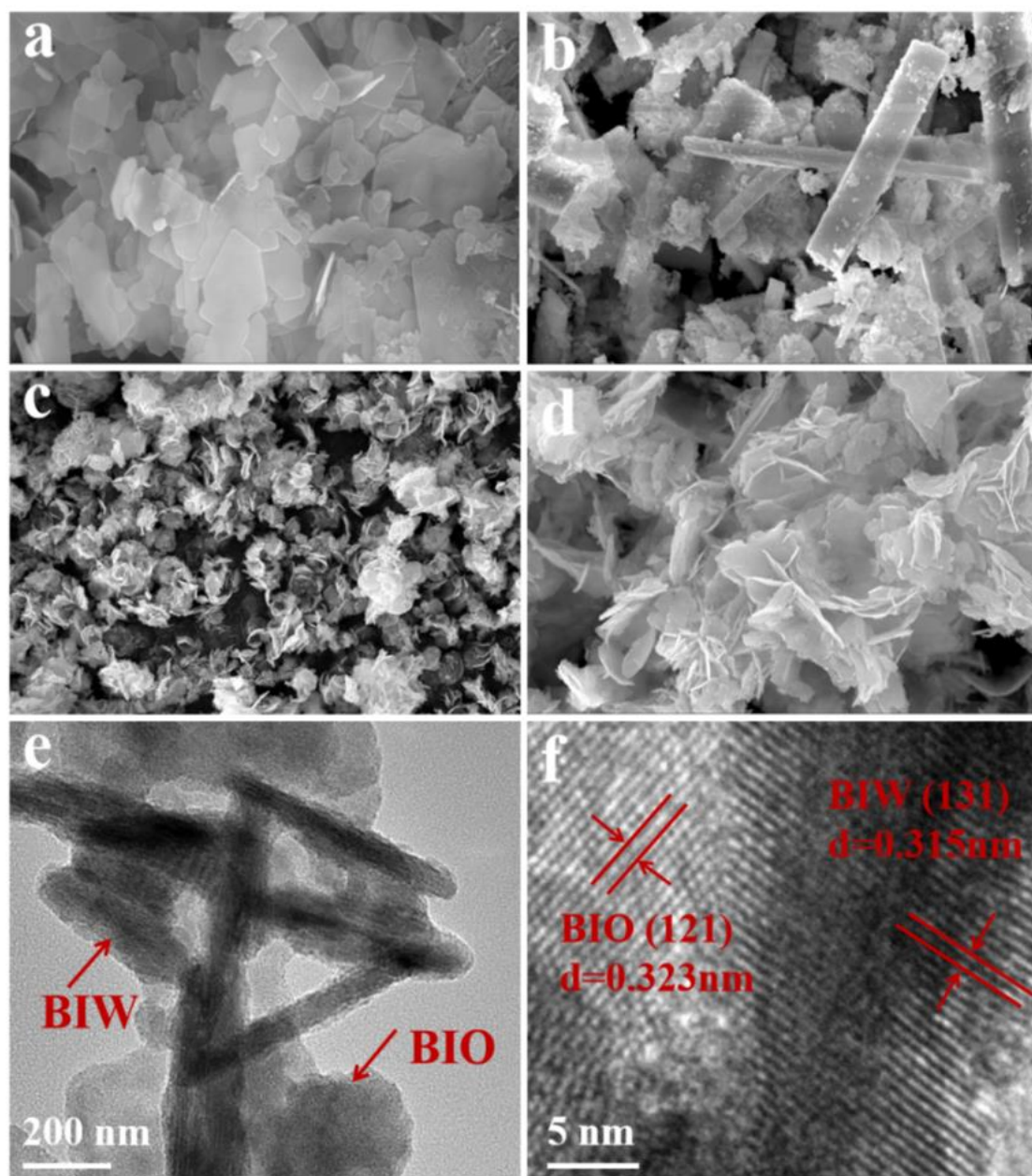


**Fig. 2.** SEM images of BIO (a), BIW (b), and BIOBIW-3 heterojunctions (c,d); TEM (a) and HRTEM (b) images of BIOBIW-3 heterojunctions.

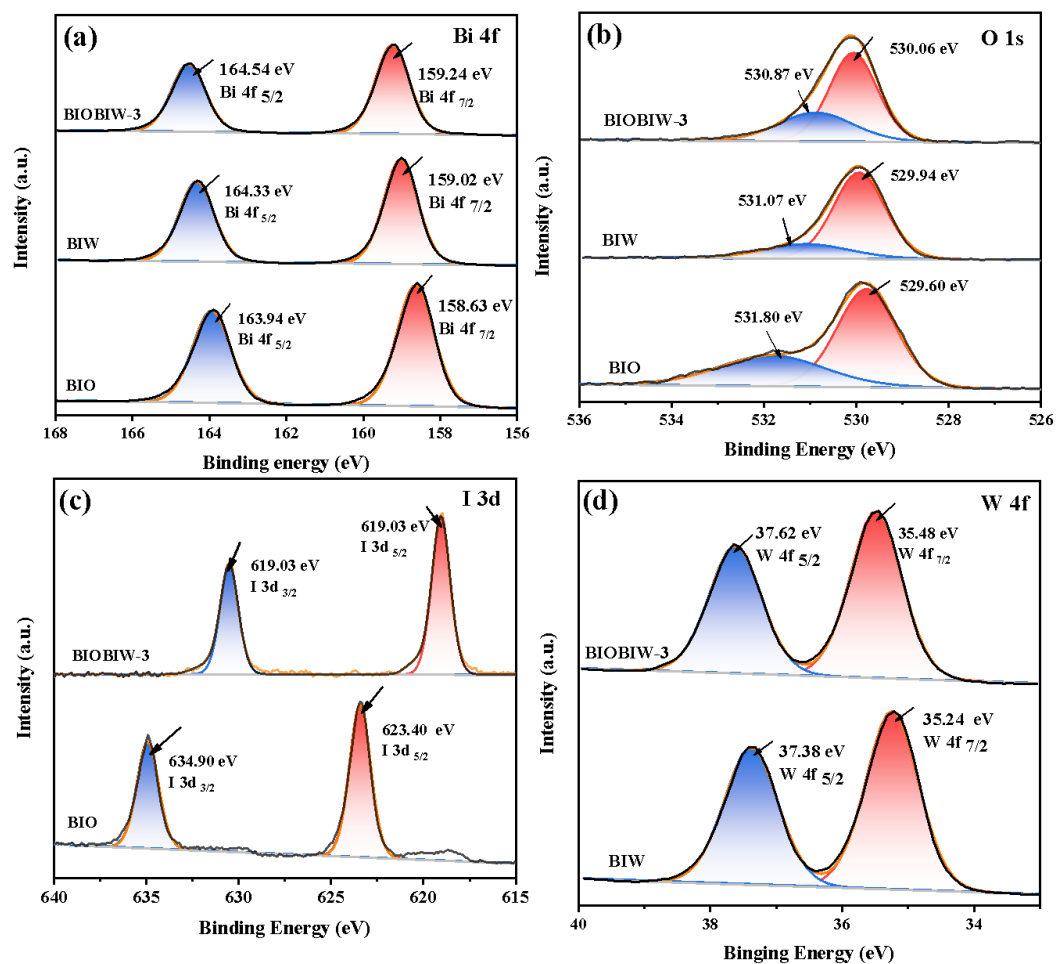


**Fig. 3.** (a) The survey XPS spectrum of BIO, BIW and BIOBIW-3 heterojunctions; (b) Bi 4f, (c) O 1s, (d) I 3d and W 4f high resolution XPS spectra of BIO, BIW and BIOBIW-3 heterojunctions.

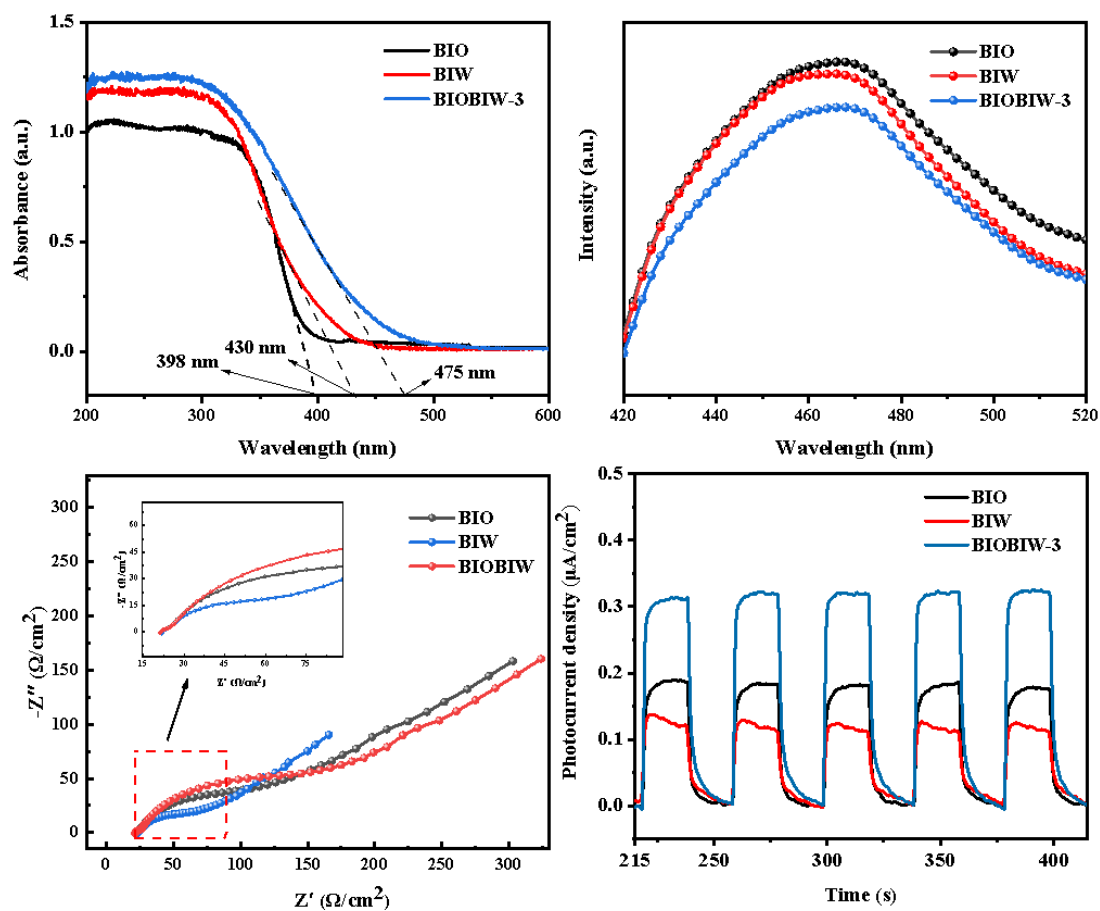


**Fig. 4.** (a) UV-Vis DRS, (b) PL spectra, (c) EIS and (d) Transient photocurrent response of BIO, BIW and BIOBIW-3 heterojunctions.

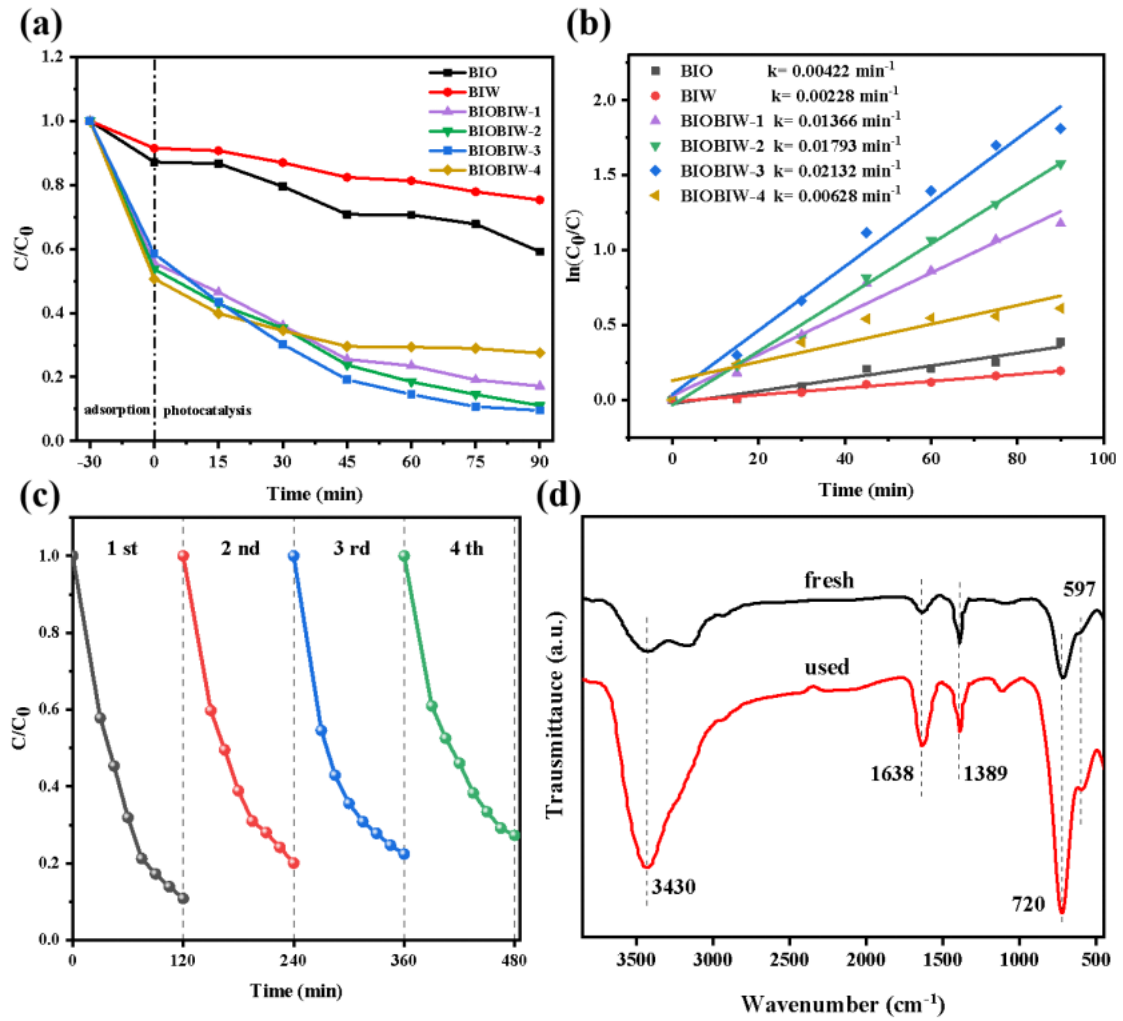


**Fig. 5.** (a) Photocatalytic degradation NOR of BIO, BIW and BIOBIW-x heterojunctions; (b) Corresponding first-order kinetics; (c) recycling stability of BIOBIW-3 heterojunctions for the degradation of NOR; (d) FTIR spectra of BIOBIW-3 heterojunctions before and after the photocatalytic reaction.

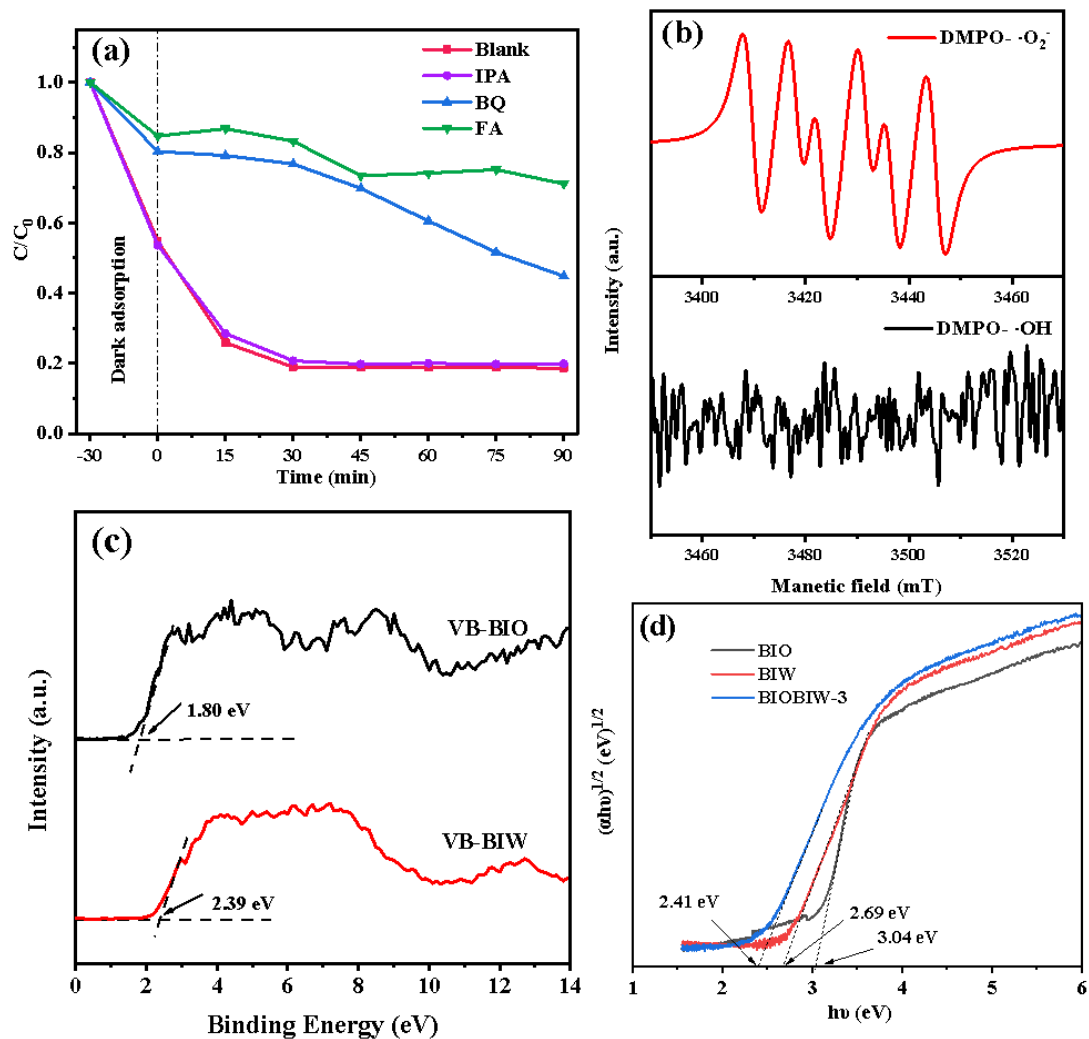


**Fig. 6.** (a) Reactive species capture experiments and (b) ESR spectra of DMPO spin-trapping over BIOBIW-3 heterojunctions; (c) VB-XPS spectrum of BIO and BIW; (d) bandgap energies of BIO, BIW and BIOBIW-3.

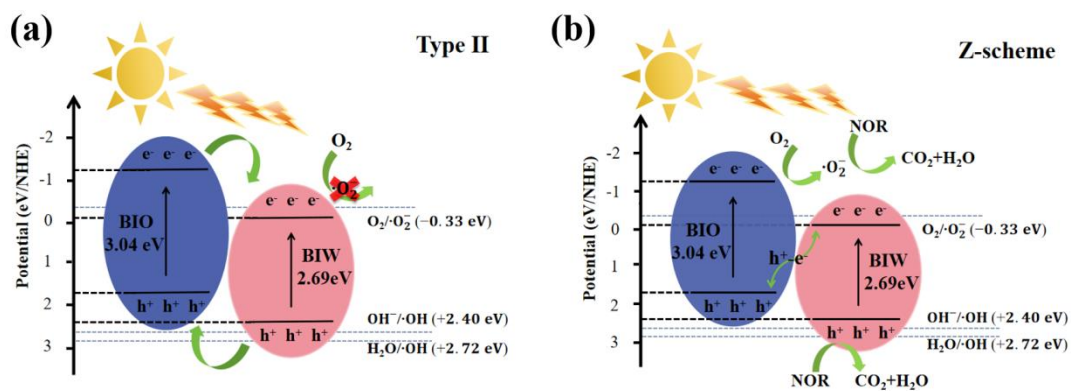


**Fig. 7.** The possible photocatalytic mechanism of BIOBIW-3 heterojunctions for NOR degradation under solar light irradiation: (a) type-II mechanism and (b) Z-scheme mechanism.