Research Article

Bi-Modified Bi$_2$WO$_6$/BiOI Heterojunction with Enhanced Visible-Light-Driven Photoactivity for Antibiotic Degradation

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A flower-like metallic Bi-modified Bi$_2$WO$_6$/BiOI heterojunction was fabricated by a two-step approach of hydrothermal method and in situ ethylene glycol reduction method. The ternary system was confirmed by structural analysis and surface and morphological studies. Compared with Bi$_2$WO$_6$, BiOI, and their binary nanomaterials, the catalyst exhibits excellent photocatalytic performance for the degradation of ciprofloxacin (CIP) and levofloxacin (LEV) under visible light irradiation. The improvement of photocatalytic performance was ascribed to the synergistic effect between metal Bi nanoparticles and Bi$_2$WO$_6$/BiOI p-n heterojunction, which enhanced the light absorption capacity and the separation efficiency of photogenerated carriers. By studying the effect of solution pH on CIP degradation, it was found that when pH = 10, the degradation efficiency of the catalyst on ciprofloxacin reached 100% within 40 min. It provides a new idea for the design and synthesis of ternary photocatalysts for purification of alkaline domestic sewage.

1. Introduction

Antibiotics are now widely used in the treatment of human and animal diseases, aquaculture, and livestock production [1]. Ciprofloxacin (CIP) and levofloxacin (LEV) are an important family of third-generation fluoroquinolones broad-spectrum antibiotics that are widely recommended by veterinarians around the world. Notably, due to the high stability and low biodegradability of antibiotics, most (75%-80%) of ciprofloxacin (CIP) and levofloxacin (LEV) are released directly into the environment through feces, causing environmental pollution [2]. CIP was detected in environmental media such as fresh water (6.5 mg/L), municipal sewage (426 mg/kg), manure (45.59 mg/kg), and agricultural soil (5.3~119.8 μg/kg) [3]. Residual CIP and other antibiotics in water streams can potentially cause harm to humans and wildlife, owing to their capability of promoting bacterial drug resistance and inducing genetic exchange [4]. Emerging pollutants based on these antibiotics have potential risks to human health including cognitive impairment, endocrine disorders, cancer, and reproductive disorders [5]. Furthermore, CIP is considered to be one of the most toxic antibiotics with low biodegradability [6]. Therefore, the simple and effective removal of CIP from the aquatic environment is of great significance. A variety of strategies, such as chemical oxidation, photocatalytic degradation, filtration, and adsorption, have been employed to remove antibiotic residues in wastewater. In comparison with traditional methods, semiconductor photocatalysis is regarded as an ideal “green” treatment for the organic pollutants, owing to its nontoxicity, low cost, high efficiency, and environmental protection features [7]. So far, there are many studies on photocatalysts for degrading antibiotics, such as Ag$_3$PO$_4$/Bi$_2$S$_3$/Bi$_2$O$_3$ [8, 9], ZnSnO$_3$ [10], BN/CdAl$_2$O$_4$ [11], rGO/Bi$_2$O$_3$Br$_2$ [12, 13], and BiOCl-Au-CdS [14, 15].

Among various semiconductor photocatalysts, Bi$_2$WO$_6$ has attracted many interests as an efficient visible-light-driven photocatalyst because of its unique electronic band structure, high chemical stability, and nontoxicity. However, the photocatalytic performance of bare Bi$_2$WO$_6$ is limited owing to its shortages such as slow carrier migration rate, quick recombination of photoexcited electron-holes, and deficiency of utilization of sunlight. In order to solve these problems, some researchers had developed a variety of strategies, such as morphology control, doping or substitution, solid
solution preparation, and composite formation [16]. Very recently, several Bi2WO6-based photocatalysts, such as Au-Bi2WO6 [17], Ba-doped Bi2WO6 [18], Bi2WO6/BiOI [19], and Bi2MoxW1-xO6 [20] had been successfully prepared, which effectively improved the electron-hole pair separation efficiency and visible light absorption efficiency of the catalysts by metal doping or forming heterojunctions with other semiconductors. It was widely accepted that the charge separation by metal doping or forming heterojunctions with other semiconductors. It was widely accepted that the charge separation by metal doping or forming heterojunctions with other semiconductors is a valid method to improve the photocatalytic performance by suppressing the recombination of photogenerated electron-holes.

Bismuth iodide oxide (BiOI) has been hugely studied due to its nontoxicity, cheapness, environmental-friendly, optical and chemical stability, and narrow band gap (about 1.8 eV) [27, 28]. Despite BiOI has these merits, its use still be limited by the rapid recombination of electron-hole pairs [29]. It has been identified that fabricating heterojunctions by coupling BiOI with other semiconductors is a valid method to improve the photocatalytic performance by suppressing the recombination of photogenerated electron-holes.

To the best of our knowledge, there are no existing reports on such a Bi-Bi2WO6/BiOI system. In this paper, Bi-modified Bi2WO6/BiOI microspheres with flower-like morphology were fabricated by a two-step approach. The photocatalytic performance was evaluated by degradation of ciprofloxacin (CIP) and levofloxacin (LEV) under visible-light irradiation. The prepared 20% Bi-Bi2WO6/BiOI composite showed markedly improvement in photocatalytic performance for the CIP and LEV degradation in comparison with bare Bi2WO6 bare BiOI, and Bi2WO6/BiOI, which was mainly ascribed to the enhancement of visible light absorption in a wider absorption range, and especially the efficient separation of photogenerated carriers on the p-n heterojunction formed between Bi2WO6 and BiOI.

2. Experimental

2.1. Preparation of Materials. Bismuth nitrate pentahydrate (Bi(NO3)3·5H2O), sodium tungstate dihydrate (Na2WO4·2H2O), potassium iodide (KI), ethylene glycol (EG), ciprofloxacin (CIP), levofloxacin (LEV), sodium sulfate (Na2SO4), sodium nitrate (NaNO3), sodium carbonate (Na2CO3), sodium chloride (NaCl), p-benzoquinone (BQ), triethanolamine (TEOA), and isopropyl alcohol (IPA) were purchased from Shanghai Chemical Reagents Co., Ltd. Ultrapure water (18.2 MΩ cm) was used in this experiment. All the reagents were analytical grade and were used without further purification.

2.1.1. Synthesis of Bi2WO6/BiOI. The Bi2WO6/BiOI composites were synthesized by hydrothermal method. In a typical synthesis, 3 mmol Bi(NO3)3·5H2O was dissolved in the mixture solution of 30 mL of deionized water and 30 mL of ethylene glycol under vigorous stirring. Then, 0.6 mmol KI and 1.2 mmol Na2WO4·2H2O were added to the above obtained solution. After stirring for 1 h, the resulting light red suspension was transferred to a 100 mL Teflon lined autoclave. The autoclave was sealed and maintained at 180°C for 12 hours, then cooled to room temperature naturally. Eventually, the resulting precipitation was collected, washed with ethanol and distilled water for three times, and dried at 60°C for 12 h. For comparison, pure Bi2WO6 and BiOI were obtained by the same synthesis procedure without the addition of KI or Na2WO4·2H2O.

2.1.2. Synthesis of Bi-Bi2WO6/BiOI. Bi-Bi2WO6/BiOI composites were prepared by deposition of Bi on Bi2WO6/BiOI surface using ethylene glycol as reducing agent. 0.2 mmol Bi(NO3)3·5H2O was dissolved in 80 mL ethylene glycol to form a transparent solution under vigorous stirring. Then, a certain amount of the prepared Bi2WO6/BiOI was added to the above transparent solution, following vigorous shaking with ultrasonic waves and then stirring for 2 h. The mixed solution was transferred to a 100 mL Teflon autoclave and then heated at 180°C for 10 h. After cooling to room temperature, the product was obtained by centrifugation, washed with ethanol and distilled water, and dried at 60°C for 12 h. By controlling the ratio of Bi(NO3)3·5H2O to Bi2WO6/BiOI, the Bi-Bi2WO6/BiOI composites containing 10.0 wt%, 20.0 wt%, and 30.0 wt% of metallic Bi, respectively, were successfully prepared. The corresponding products were labeled as 10.0% Bi-Bi2WO6/BiOI, 20.0% Bi-Bi2WO6/BiOI, and 30.0% Bi-Bi2WO6/BiOI, respectively.

2.2. Characterization. The X-ray power diffraction (XRD) of the products was analyzed by using a Bruker D8 Focus X-ray diffractometer (Bruker, Germany) with Cu-Kα radiation (λ = 0.154178 nm). The product morphology was analyzed by field emission scanning electron microscopy (FESEM, ZEISS ULTRA55, Germany). Transmission electron microscopy (TEM, Japan) and high-resolution TEM (HRTEM) measurements were examined via a JEM-2100F microscope. UV-vis diffuse reflectance spectra of the samples were obtained on an UV-vis spectrophotometer (Cary 5000, Shimadzu, Japan). X-ray photoelectron spectroscopy (XPS) were acquired using the ESCALAB 250 spectrometer.
Figure 3: (a) TEM image, (b) HRTEM image of 20% Bi-Bi$_2$WO$_6$/BiOI, and (c–g) the STEM-EDS elemental mapping images of Bi, W, I, and O, respectively.
Figure 4: Continued.
(Thermo, USA) with Al Ka (1486.6 eV) line to get the elements and chemical state. The photoluminescence (PL) emission spectra of the products were carried out on a RF-5301PC fluorescence spectrophotometer (Shimadzu, Japan). The photocurrent response and electrochemical impedance spectra (EIS) measurements were carried out in a conventional three-electrode system with a 0.1 M Na₂SO₄ electrolyte solution by using an electrochemical system (SP-150, France).

2.3. Photoelectrochemical Measurement. Transient photocurrent response and electrochemical impedance spectroscopy (EIS) were measured by electrochemical workstation (CHI660D) to analyze the photochemical properties of the photocatalyst. The Ag/AgCl and Pt electrodes were used as the reference and counter electrodes, respectively. The working electrode was prepared by coating the sample on a fluorine-doped tin oxide (FTO) glass. A 300 W Xe lamp with a cutoff filter (λ > 420 nm) was used as the light source, and 0.1 M Na₂SO₄ solution was used as the electrolyte.

2.4. Photocatalytic Activity. The photocatalytic activities of the samples were assessed by degradation of ciprofloxacin solution.
(CIP, 20 mg/L) and levoﬂoxacin solution (LEV, 20 mg/L) under visible-light irradiation. Visible-light was provided by a 300 W Xe lamp with a cutoff filter ($\lambda > 420$ nm). 50 mg photocatalyst was added to a glass reactor containing 50 mL CIP solution, and then, the suspensions were stirred for 1 h under dark conditions to reach the adsorption-desorption equilibrium. Experiment of LEV degradation was carried out under the same conditions, in which 40 mg photocatalyst was added into 50 mL of LEV solution. At certain intervals, 3 mL of the reaction solution was gathered and centrifugated to remove the catalyst. Then, the CIP and LEV concentration was measured by UV-vis spectrophotometer (TU-1901).

3. Results and Discussion

3.1. Morphology and Structure Analysis. The crystal structures of the as-prepared BiOI, Bi$_2$WO$_6$, Bi$_2$WO$_6$/BiOI, and Bi-Bi$_2$WO$_6$/BiOI photocatalysts were characterized by XRD analysis. As displayed in Figure 1, BiOI sample was indexed to the tetragonal phase BiOI (JCPDS Card No.10-0445) [30]. For pure Bi$_2$WO$_6$, Bi$_2$WO$_6$/BiOI, and Bi-Bi$_2$WO$_6$/BiOI samples, the distinct diffraction peaks with 2$\theta$ values of 28.3°, 32.9°, 47.1°, and 55.8° were perfectly indexed to the (1 3 1), (0 0 2), (2 0 2), and (3 3 1) crystal planes of rhombic phase Bi$_2$WO$_6$ (JCPDS Card No.39-0256) [31]. For Bi$_2$WO$_6$/BiOI samples, the characteristic peaks of BiOI were not observed, indicating that BiOI was highly dispersed on the surface of Bi$_2$WO$_6$. In the case of Bi-Bi$_2$WO$_6$/BiOI, several new diffraction peaks appeared at 2$\theta = 27.2^\circ$, 38.0°, and 39.6°, which can be attributed to the (0 1 2), (1 0 4), and (1 1 0) crystal planes of metal Bi (JCPDS Card No. 44-1246) [32], suggesting that Bi-modified Bi$_2$WO$_6$/BiOI composites were successfully fabricated. With the increment of the ratio of Bi(NO$_3$)$_3$·5H$_2$O to Bi$_2$WO$_6$/BiOI, the density of diffraction peaks of metallic Bi becomes stronger and narrower, indicating bigger metallic Bi nanoparticles in 30% Bi-Bi$_2$WO$_6$/BiOI than in 10% Bi-Bi$_2$WO$_6$/BiOI.

The morphology of the as-prepared BiOI, Bi$_2$WO$_6$, Bi$_2$WO$_6$/BiOI, and 20% Bi-Bi$_2$WO$_6$/BiOI photocatalysts were characterized by FESEM. As shown in Figure 2(a), the bare Bi$_2$WO$_6$ exhibited a 3D microflower structure with a diameter of 3 $\mu$m, which was composed of loosely packed 35 nm thick nanosheets with much interspace on the surface. Figure 2(b) showed that 2D BiOI nanosheets with a thickness of about 40 nm aggregated into 3D BiOI flower-like microspheres with a diameter of about 2.7 $\mu$m. The Bi$_2$WO$_6$/BiOI heterojunction and 20% Bi-

![Figure 6: (a) N$_2$ adsorption-desorption isotherms and (b) pore size distribution of the BiOI, Bi$_2$WO$_6$, Bi$_2$WO$_6$/BiOI, and Bi-Bi$_2$WO$_6$/BiOI samples.](image-url)

**Table 1: The pore structural parameters of samples.**

| Sample          | $S_{BET}$ (g/cm$^2$) | Average pore size (nm) | Pore volume (cm$^3$/g) |
|-----------------|----------------------|------------------------|------------------------|
| BiOI            | 28.7                 | 10.94                  | 0.15                   |
| Bi$_2$WO$_6$    | 27.1                 | 7.54                   | 0.12                   |
| Bi$_2$WO$_6$/BiOI | 30.6                 | 12.80                  | 0.23                   |
| Bi-Bi$_2$WO$_6$/BiOI | 38.5                 | 16.12                  | 0.28                   |
Figure 7: Continued.
Bi$_2$WO$_6$/BiOI heterojunction presented the similar morphologies of a flower-like layered structure consisted of 20 nm thick nanosheets (Figures 2(c) and 2(d)). However, the surface of 20% Bi-Bi$_2$WO$_6$/BiOI (Figure 2(d)) became rough, indicating that some Bi nanoparticles were formed on the petals.

Figure 3 showed the high-resolution TEM image of the 20% Bi-Bi$_2$WO$_6$/BiOI heterojunction. It can be seen that 20% Bi-Bi$_2$WO$_6$/BiOI sample were composed of little 2D interlaced nanosheets (Figure 3(a)), which was consistent with the above FESEM images (Figure 2(d)). Three different lattice fringe spacings were detected in TEM imagine of 20% Bi-Bi$_2$WO$_6$/BiOI heterojunction (Figure 3(b)), implying that Bi, Bi$_2$WO$_6$, and BiOI were well combined and closely contacted, resulting in the formation of a heterostructure. The interplanar spacings of 0.315 nm, 0.199 nm, and 0.328 nm corresponded to the (1 3 1) crystal plane of Bi$_2$WO$_6$, the (2 0 0) crystal plane of BiOI, and the (0 1 2) crystal plane of Bi [33, 34], respectively. In addition, the STEM mapping shown in Figures 3(d)–3(g) verified that 20% Bi-Bi$_2$WO$_6$/BiOI was mainly consisted of four elements (Bi, W, I, and O), suggesting that 20% Bi-Bi$_2$WO$_6$/BiOI heterojunction was successfully synthesized.

The elemental composition and chemical state of 20% Bi-Bi$_2$WO$_6$/BiOI was studied by using XPS technique.
The XPS survey spectrum (Figure 4(a)) showed the presence of Bi, W, I, and O elements in 20% Bi-Bi₂WO₆/BiOI. Figure 4(b) demonstrated two peaks at 164.6 eV and 159.3 eV, which were attributed to the Bi 4f 5/2 and Bi 4f 7/2 in the Bi³⁺ chemical state [19], respectively. Two peaks centered at 162.2 eV and 156.9 eV were related to the metal Bi⁰ [35]. As shown in Figure 4(c), there were two peaks located at 35.6 eV and 37.7 eV, which corresponded to the W 4f 5/2 and W 4f 7/2 of the W⁶⁺ chemical state [36], respectively. The binding energy of I in BiOI fit into two peaks centered at 619.3 eV and 630.8 eV (Figure 4(d)), corresponding to I 3d 3/2 and W 4f 5/2 of the W⁶⁺ chemical state [37], respectively. The XPS spectrum of O 1s can be fitted to two peaks (Figure 4(e)), which were located at 530.2 eV and 531.4 eV, corresponding to the lattice oxygen and the oxygen adsorbed on the surface [38], respectively.

3.2. Optical Properties. The optical properties of the as-prepared samples were evaluated by UV-Vis diffuse reflectance spectroscopy.

As displayed in Figure 5(a), the absorption edge of Bi₂WO₆ was around 450 nm, indicating that it can be excited in the visible-light range. It was obvious that after depositing metallic Bi, 20% Bi-Bi₂WO₆/BiOI displayed higher absorption capacity of visible-light in comparison with the Bi₂WO₆/BiOI heterojunction. The band gap energy (Eg) of the sample can be calculated by Kubelka-Munk equation [39]:

\[
\alpha(h\nu) = A(h\nu - E_g)^{n/2},
\]

where \(E_g\) represented the band gap energy, \(h\nu\) represented Planck constant, \(\nu\) represented the frequency of light, \(A\) represented the absorption coefficient, \(n\) represented the proportionality constant, and the value of \(n\) depended on the type of photocatalyst transition (direct transition when \(n = 1\), indirect transition when \(n = 4\)). The \(n\) value of Bi₂WO₆ and BiOI was 4 [40]. According to the Tauc curve (Figure 5(b)), the band gap values of Bi₂WO₆ and BiOI were 2.73 eV and 1.72 eV, respectively.

3.3. BET Characterization. The specific surface area is an important parameter to characterize photocatalytic materials. The specific surface areas of BiOI, Bi₂WO₆, Bi₅WO₁₆/BiOI, and Bi-Bi₂WO₆/BiOI powders were determined by low-temperature N₂ adsorption method, and results are shown in Figure 6. It can be seen that the nitrogen adsorption-desorption isotherm curves of the BiOI, Bi₂WO₆, Bi₅WO₁₆/BiOI, and Bi-Bi₂WO₆/BiOI samples were characterized by the type-IV adsorption isotherm according to the IUPAC standard (Figure 6(a)).

Figure 6(b) shows the pore size distribution curves of BiOI, Bi₂WO₆, Bi₅WO₁₆/BiOI, and Bi-Bi₂WO₆/BiOI. The BET surface areas and pore structural parameters of BiOI, Bi₂WO₆, Bi₅WO₁₆/BiOI, and Bi-Bi₂WO₆/BiOI are listed in Table 1. The BET surface area of Bi-Bi₂WO₆/BiOI is higher than that of BiOI, Bi₂WO₆, Bi₅WO₁₆/BiOI, which means that Bi-Bi₂WO₆/BiOI photocatalyst can provide more photocatalytic reaction active sites and have a stronger ability to absorb visible-light during the photocatalytic degradation process.

3.4. Photocatalytic Degradation of CIP and LEV

3.4.1. Photocatalytic Performance. The photocatalytic activity of the prepared photocatalyst was evaluated in detail for the degradation of CIP and LEV under visible-light irradiation. The mixture of catalyst and CIP or LEV aqueous was first stirred for 60 min in dark at room temperature to assure the adsorption equilibrium was reached (Figure 7), which is one of the important parameters influencing the photocatalytic process. It has been widely acknowledged that the adsorption capacity of catalysts plays an important role in their practical applications in the treatment of wastewater containing trace amounts of organic contaminants. Generally, the larger the specific surface area of the catalyst, the larger the adsorption capacity, which can provide more active sites. When the adsorption of CIP and LEV on photocatalyst reached the adsorption-desorption equilibrium, the adsorption capacity \(Q_e\) (mg/g) can be calculated by the following equation:

\[
Q_e = \frac{V(C_0 - C_e)}{m},
\]

where \(C_0\) and \(C_e\) are the initial concentration and the equilibrium concentration of CIP or LEV (mg/L), respectively. \(V\) is the volume (L) of the CIP or LEV aqueous solution, and \(m\) is the weight (g) of the photocatalyst. The calculated adsorption capacity of the Bi-Bi₂WO₆/BiOI sample for CIP or LEV molecules is higher than that of the BiOI, Bi₂WO₆ and Bi₂WO₆/BiOI sample, which is consistent with BET results. As shown in Figure 7(a), the CIP degradation efficiency of
BiOI, Bi$_2$WO$_6$, and Bi$_2$WO$_6$/BiOI heterostructure was 11.1%, 42.7%, and 76.7% under visible light irradiation for 80 min, respectively. In comparison, after the introduction of appropriate amount of metallic Bi, the degradation efficiency of CIP was significantly improved, and the degradation efficiency of 20% Bi-Bi$_2$WO$_6$/BiOI was the highest at 96.0%. Figure 7(c) showed that in the presence of 20% Bi-Bi$_2$WO$_6$/BiOI, 83.3% LEV could be degraded after 60 minutes of visible-light irradiation.

The pseudo first-order reaction rate constant ($k$) of photocatalytic degradation of CIP and LEV was calculated by the following formula:

$$\ln\left(\frac{C_t}{C_0}\right) = -kt, \quad (3)$$

where $C_t$ and $C_0$ are the concentration of CIP at time $t$ and 0, respectively.

In Figure 7(b), the apparent reaction rate constant of 20% Bi-Bi$_2$WO$_6$/BiOI for the degradation of CIP was 0.0335 min$^{-1}$, which was about 7.28 times and 111.67 times as high as that of Bi$_2$WO$_6$ (0.0046 min$^{-1}$) and BiOI (0.0003 min$^{-1}$). Accordingly, the photodegradation rate constant (0.0206 min$^{-1}$) of LEV with 20% Bi-Bi$_2$WO$_6$/BiOI was also the highest (Figure 7(d)). The mineralization of organic pollutants is an important aspect of pollutant treatment. The total organic carbon value is the main index of the mineralization of organic species. In this paper, the TOC removal efficiency of CIP and LEV over 20% Bi-Bi$_2$WO$_6$/BiOI was investigated (Figure 8). After irradiation for 80 and 60 min, the removal rate of TOC reached about 33% and 15%, respectively, which proved that 20% Bi-Bi$_2$WO$_6$/BiOI had certain mineralization ability for CIP and LEV.

In addition, a comparison was made between 20% Bi-Bi$_2$WO$_6$/BiOI and other photocatalysts reported in literature in the degradation efficiency of CIP or LEV (Table 2).

### Table 2: Summary of the photocatalytic degradation of LEV or CIP by different photocatalysts.

| Photocatalysts                      | $C_{photocatalysts}$ (g/L) | $C_{pollutants}$ (mg/L) | Efficiency (%) | Rate constant (min$^{-1}$) | References |
|-------------------------------------|-----------------------------|-------------------------|----------------|-----------------------------|------------|
| CFs/MoS$_2$/UiO-66-NH$_2$           | 1.5                         | 20                      | LEV: 88.4 (120 min) |                             | [41]       |
| CdS/Bi$_2$GeO$_{20}$                | 0.5                         | 10                      | LEV: 80 (120 min) | 0.0340                      | [42]       |
| BiOI/rGO                            | 1                           | 20                      | LEV: 51 (120 min) | 0.00612                     | [43]       |
| BiOI-MWCNT                          | 1                           | 20                      | LEV: 46.1 (60 min) | 0.00538                     | [44]       |
| Ag$_2$O/Bi$_{12}$GeO$_{20}$         | 0.5                         | 10                      | CIP: 70 (120 min) |                             | [45]       |
| CuBi$_2$O$_6$/Bi$_2$O$_3$ @rGO      | 1                           | 10                      | CIP: 92 (100 min) | 0.0182                      | [46]       |
| Bi$_2$O$_4$/UiO-66-NH$_2$           | 0.5                         | 10                      | CIP: 82.2 (120 min) | 0.0136                      | [47]       |
| CuBi$_2$O$_4$/Bi/BiOBr              | 1                           | 10                      | CIP: 91 (120 min) | 0.0201                      | [49]       |
| CeO$_2$-Ag/AgBr                     | 1                           | 10                      | CIP: 90 (120 min) | 0.0160                      | [50]       |
| BiOBr/Bi$_2$WO$_6$                  | 0.5                         | 10                      | CIP: 74.2 (180 min) | 0.00656                     | [51]       |
| p-Ag$_2$S$_2$O$_7$/n-Bi$_2$WO$_6$   | 0.625                       | 20                      | CIP: 94.8 (120 min) | 0.0217                      | [52]       |
| Ti$_3$C$_2$-Bi/BiOCl                | 1                           | 20                      | CIP: 89 (100 min) | 0.0223                      | [53]       |
| Bi$_2$TaO$_7$-CdS                   | 0.6                         | 5                       | CIP: 76.5 (60 min) | 0.0543                      | [54]       |
| Biochar @ZnFe$_2$O$_4$/BiOBr        | 0.5                         | 15                      | CIP: 84 (60 min) |                             | [55]       |
| Bi-Bi$_2$WO$_6$/BiOI                | CIP: 1 LEV: 0.8              | CIP, 20 LEV:20          | CIP: 96 (80 min) | CIP: (0.0355)                | This work  |
|                                    | LEV: 83.3 (60 min)          |                          | LEV: (0.0206)    |                            |            |
Figure 9: Continued.
order of photodegradation efficiency was NaNO₃ > NaCl > Na₂SO₄ > Na₂CO₃. Among them, NaNO₃, NaCl, and Na₂SO₄ had a certain inhibitory effect, which may be due to the competitive adsorption between these three ions (NO₃⁻, Cl⁻, and SO₄²⁻) and CIP molecules, resulting in the reduction of available active sites [37]. The presence of Na₂CO₃ significantly hindered the degradation efficiency of CIP, because CO₃²⁻ was the scavenger of •OH and h⁺. According to the subsequent result of trapping experiments, only a small amount of •OH was produced in the photodegradation process, so CO₃²⁻ reduced the photocatalytic activity by consuming h⁺ [57].

3.4.4. Effect of pH. The pH value of solution is a significant operating parameter in practical application, since the solution pH can affect the surface property of photocatalyst, the ionization state of pollutants, and the formation of active species [58]. Therefore, the effect of pH value on the degradation efficiency of CIP over the 20% Bi-Bi₂WO₆/BiOI photocatalyst was systematically investigated. Three pathways have been proposed in previous studies on photolytic degradation of CIP. (i) Photo-substitution of the fluorine atom by a hydroxyl group is expected to be a quite common result in neutral and moderately basic solutions or (ii) defluorination which occurs in neutral solutions and (iii) fluorine conservation under strongly acidic conditions. During the photocatalytic reaction, the first reaction step is mainly defluorination, followed by degradation at the CIP piperazine ring [59]. As shown in Figure 9(c), at pH = 3.3, due to the conservation of fluorine in CIP under acidic conditions, the photosubstitution of fluorine competes with the absorption of light by the photocatalyst, resulting in ciprofloxacin not easily excited by ultraviolet radiation, reducing the degradation of ciprofloxacin. With the increase of pH value, the CIP degradation pathway changed from pathway (iii) to pathway (i), and the CIP adsorption capacity of 20% Bi-Bi₂WO₆/BiOI gradually increased and reached 80% when the solution is under alkaline conditions (pH = 10.0). At varied pH conditions, the surface charge state of the semiconductor and the dissociation degree of the solution may be changed, which ultimately would affect the photocatalytic performance [60].

3.4.5. Photoelectrochemical Properties. The separation efficiency and migration rate of photogenerated carriers play a major role in photocatalytic degradation. Therefore, the transient photocurrent response was used to research the separation efficiency of photogenerated carriers. It can be observed in Figure 10(a). The transient photocurrent densities of Bi₂WO₆, BiOI, and Bi₂WO₆/BiOI heterostructures were 0.22 μA/cm², 0.11 μA/cm², and 0.34 μA/cm², respectively. In comparison, the photocurrent density of 20% Bi-Bi₂WO₆/BiOI composites was significantly increased to 0.43 μA/cm², indicating that the charge carrier separation of 20% Bi-Bi₂WO₆/BiOI heterostructures was greatly enhanced.

Electrochemical impedance was another technique used to evaluate the electrochemical properties of photocatalysts. It is well-accepted that the smaller arc diameter in Nyquist plots indicate the smaller the electron transport resistance and the higher the electron transferred efficiency. EIS measurements were carried out to characterize the as-prepared samples. As shown in Figure 10(b), among all the tested photocatalysts (Bi₂WO₆, BiOI, Bi₂WO₆/BiOI heterojunctions, and 20% Bi-Bi₂WO₆/BiOI), the arc radius of 20% Bi-Bi₂WO₆/BiOI composites was the smallest, indicating lowest electron transfer impedance under visible light irradiation.
Figure 10: Continued.
To further prove that ternary heterostructures were beneficial to the separation of photogenerated carriers, the recombination rate of photogenerated electrons and holes was measured by photoluminescence (PL) spectroscopy. As displayed in Figure 10(c), the corresponding order of PL intensity was BiOI > Bi2WO6 > Bi2WO6/BiOI > 20% Bi-Bi2WO6/BiOI composites, indicating that 20% Bi-Bi2WO6/BiOI had the lowest recombination rate of photogenerated electrons and holes. After the introduction of Bi nanoparticles, the separation effect of photogenerated electrons-holes in 20% Bi-Bi2WO6/BiOI composites was markedly enhanced, which implied that the recombination rate of electron-hole pairs can be effectively suppressed through the formation of heterojunction among Bi, Bi2WO6, and BiOI.

3.4.6. Photocatalytic Mechanism. It is vitally important to identify the main active oxidant in the photocatalytic reaction process for better understanding the mechanism. In order to distinguish the roles of different active components in the photocatalytic reaction process, three scavengers of active species, triethanolamine (TEOA), p-benzoquinone (BQ), and iso-propanol (IPA), were used to trap hole (h+), superoxide radical (•O2−), and hydroxyl radical (•OH), respectively. As shown in Figure 11, the degradation efficiency of CIP was slightly depressed by the addition of IPA. When BQ and TEOA were added into the solution, the degradation efficiency was significantly reduced, and the order of inhibition degree was BQ > TEOA. These results strongly suggested that h+ and •O2− played a dominant role in the photocatalytic process of CIP over 20% Bi-Bi2WO6/BiOI heterojunction.

In order to further understand the separation process of photogenerated carriers of 20% Bi-Bi2WO6/BiOI composites, based on the results of DRS, the band edge positions of the conduction band (CB) and valence band (VB) values of BiOI and Bi2WO6 photocatalysts can be evaluated using the empirical formula:

$$E_{CB} = X - E_e - 0.5E_g,$$

$$E_{VB} = E_{CB} + E_g,$$

where $E_{VB}$ is the valence band (VB) edge potential, $E_{CB}$ is the conduction band (CB) edge potential, $X$ is electronegativity of the semiconductor (which is the geometric average of the absolute electronegativity of the constituent atoms), $E_g$ is the band gap energy of the semiconductor, and $E_e$ is the energy of free
electrons on the hydrogen scale ($E_e = 4.5\, eV$) [61]. The electronegativity of BiOI and Bi$_2$WO$_6$ was reported to be 5.99 eV and 6.36 eV, respectively [62, 63]. Herein, on the basis of the above equation, the $E_{CB}$ and $E_{VB}$ of BiOI were determined to be 0.63 eV and 2.35 eV, respectively, while the $E_{CB}$ and $E_{VB}$ of Bi$_2$WO$_6$ were 0.50 eV and 3.23 eV, respectively.

According to the above results, it can be inferred that the introduction of metallic Bi$^0$ nanoparticles on Bi$_2$WO$_6$/BiOI surface led to significantly improve the photocatalytic performance for CIP degradation. On the basis of various characterization and experimental results, a possible mechanism for photodegrading CIP and LEV of 20% Bi-Bi$_2$WO$_6$/BiOI heterojunctions was proposed, as indicated in Figure 12. The Fermi level of Bi$^0$ (approximately -0.17 eV) is more negative than the CB independent of Bi$_2$WO$_6$ and BiOI, so the photogenerated charge of Bi$^0$ can be easily transferred to BiOI or Bi$_2$WO$_6$ [64]. According to literature reports, Bi$_2$WO$_6$ is a typical n-type semiconductor, and BiOI is a typical p-type semiconductor, and the combination between n-type Bi$_2$WO$_6$ and p-type BiOI will result in the formation of p-n heterojunctions [65]. Although the band positions of independent Bi$_2$WO$_6$ or independent BiOI was not matched with each other before contact, by combining them, the band of BiOI would move up along the Fermi level and the band of Bi$_2$WO$_6$ would move down along the Fermi level until their Fermi levels reached equilibrium. Thus, the photogenerated holes ($h^+$) in Bi$_2$WO$_6$ can be transferred to the valence band (VB) of BiOI. Meanwhile, the photogenerated electrons ($e^-$) in BiOI can be transferred to the conduction band (CB) of Bi$_2$WO$_6$, thus achieving effective charge separation. In addition, the $E_{CB}$ value of bare Bi$_2$WO$_6$ (0.5 eV) was more positive than the potential of O$_2$/•O$_2^-$ (-0.046 eV) [66], so O$_2$ cannot be reduced to •O$_2^-$. When 20% Bi-Bi$_2$WO$_6$/BiOI ternary heterojunction was used as a photocatalyst, in which BiOI can serve as a sensitizer, the $e^-$ in VB of BiOI can be excited to a higher potential edge (-0.60 eV) under visible light [67, 68]. Thus, the electrons generated from 20% Bi-Bi$_2$WO$_6$/BiOI ternary heterojunction can react with O$_2$ to produce •O$_2^-$. Simultaneously, the $E_{VB}$ value of BiOI (2.36 eV) was lower than the potential of H$_2$O/•OH (2.72 eV) [33], so $h^+$ can oxidize OH$^-$ or H$_2$O to produce •OH, but $h^+$ can react directly with pollutants. Therefore, the active species trapping experiments suggested that •O$_2^-$ and $h^+$ played a major role in the photocatalytic process. Owing to the surface plasmon resonance (SPR) effect, the introduction of plasma Bi$^0$ will bring about more electron-hole pairs under visible-light irradiation [60]. The synergistic effect between Bi$^0$ and p-n Bi$_2$WO$_6$/BiOI heterojunction can realize the effective generation, separation, and transfer of photogenerated charge and results in significant improvement of the photocatalytic performance.

3.4.7. Reusability and Stability. The reusability and stability of photocatalyst is a crucial factor for its practical applications. Therefore, the stability of the as-prepared 20% Bi-Bi$_2$WO$_6$/BiOI was investigated under visible-light irradiation. As depicted in Figure 13, there was no significant inactivation of photocatalytic performance after four recycling experiments, indicating that 20% Bi-Bi$_2$WO$_6$/BiOI had good stability. Based on the above results, 20% Bi-Bi$_2$WO$_6$/BiOI composites can be used as photostable catalysts for environmental remediation.

![Figure 12: Mechanism of charge transfer pathway in 20% Bi-Bi$_2$WO$_6$/BiOI under visible-light irradiation.](image12)

![Figure 13: Recycling photocatalytic experiment of CIP degradation over 20% Bi-Bi$_2$WO$_6$/BiOI photocatalyst under visible light irradiation.](image13)
4. Conclusion

In conclusion, we successfully prepared a flower-like Bi-Bi$_2$WO$_6$/BiOI heterojunction for the degradation of CIP and LEV. The photocatalytic experiments indicated that the 20% Bi-Bi$_2$WO$_6$/BiOI exhibited the highest photocatalytic activity among all samples. After 80 min of visible-light irradiation, the photocatalytic degradation efficiency of CIP could reach 96%, while that of LEV could also reach 83.3% after 60 min of visible-light irradiation. The enhancement of the photocatalytic performance of Bi-Bi$_2$WO$_6$/BiOI heterojunction was mainly ascribed to the enhancement of visible light absorption in a wider absorption range and especially the efficient separation of photogenerated carriers on the p-n heterojunction formed between Bi$_2$WO$_6$ and BiOI. In addition, scavenging experiments of active species showed that h$^+$ and •O$_2^-$ radicals played a key role in the photodegradation reaction.

Data Availability

The dataset supporting the conclusions of this article is included within the article.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Authors’ Contributions

Xia Zou and Sisi Wang contributed equally to this work.

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