

Article

Insights into the Mechanism of the Bi/BiVO₄ Composites for Improved Photocatalytic Activity

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Abstract: The increasing concentration of residual ciprofloxacin (CIP) can cause potential harm to the environment. Photocatalysis has been regarded as an effective method for the degradation of CIP. Bi/BiVO₄ with excellent photocatalytic performance was synthesized partial reduction with NaBH₄. The structure, morphology, composition, and optical performance of BiVO₄ and Bi/BiVO₄ were characterized by a variety of techniques. The results showed that the Bi/BiVO₄ exhibits high photocatalytic activity in the degradation of CIP. Comparison of BiVO₄ and Bi/BiVO₄ has lower photoluminescence intensity and higher photocurrent responses intensity. The introduction of Bi made Bi/BiVO₄ have a higher charge separation efficiency and generate more active free radicals. In addition, the radical trapping experiments revealed that superoxide free radicals and holes were the main active free radicals during the degradation of CIP. The pathway of CIP degradation was investigated through high performance liquid chromatography-mass spectrometry, and a possible degradation mechanism was proposed.

Keywords: BiVO₄; bismuth; photocatalysis; CIP



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1. Introduction

Antibiotic drugs are broadly applied for medical treatment, prevention of animal diseases, and bactericides in agriculture. Ciprofloxacin (CIP), a third-generation quinolone antibacterial drug, is widely used due to its strong bactericidal effect [1]. However, residual CIP is discharged into the natural environment through various pathways, such as medical treatment wastewater, livestock wastewater, and human excretion [2]. Although only a small amount of CIP (ug/L–mg/L range) can be detected in surface water [3], it still pollutes the environment and generates drug-resistant bacteria [4–7]. Bioaccumulation increases the content of CIP in livestock and poses an adverse health risk for people who consume its meat. Furthermore, the CIP removal rate through the conventional methods, such as the activated sludge process, absorption, and microbial degradation, is limited [8]. Therefore, an effective technology must be developed to solve the residual CIP pollution.

In recent years, photocatalytic degradation of residual drugs has become a topic of interest because of its fleet degradation, low cost, and high degree of mineralization of pollutants [9–11]. BiVO₄ has the potential to be a green photocatalyst due to its great thermostability, good physicochemical stability, nontoxicity, and simplicity. A narrow band gap and suitable band positions of BiVO₄ enable it to have excellent visible light response and degradation ability of organic pollutants [12–14]. Nevertheless, the photocatalytic performance of BiVO₄ is still low due to the high recombination rate of photogenerated carriers [15]. Different strategies were developed, such as ion doping [16,17], heterojunction [18,19], and morphology control [20], to improve the separation rate of photogenerated charges. The combination of noble metal and semiconductor is considered an efficient way

to improve the photocatalytic activity. The main aspects to improve the photocatalytic performance are localized surface plasmonic resonance (LSPR) and Schottky barrier formation. The LSPR effect of a noble metal can expand the light-absorption ranges of a photocatalyst and construct Schottky barrier formation to suppress the recombination of photogenerated charges. [21]. In recent years, several synthetic materials that show heightened photocatalytic activity with noble metal acting as a cocatalyst have been manufactured, such as Au/BiVO₄ [22] and Ag/BiVO₄ [23]. However, the development is limited for the high price and shortage of noble metal. Non-noble metal bismuth (Bi) has attracted extensive attention for its narrow band gap, high carrier mobility, and LSPR effect [24,25]. Studies reported that the photocatalytic performance of a material could be significantly improved by the introduction of Bi [26–28]. Wang et al. [27] constructed Bi/Bi₃NbO₇ heterojunction by a simple two-step wet chemical method. The transfer and separation of photogenerated charges were promoted due to the strong covalent interaction between Bi atoms and Bi–O layer, and the degradation efficiency of CIP was improved. Lai et al. [29] prepared Bi-decorated TiO₂ for photocatalytic toluene degradation. Metallic Bi modification increased the ability of the photocatalyst to capture O₂, which accelerated the degradation efficiency of toluene.

Herein, Bi/BiVO₄ was prepared using an in situ chemical reduction at room temperature for the degradation of CIP. Metallic Bi with LSPR effect and the ability to adsorb O₂ was generated in situ on the defective BiVO₄, which was conducive to the generation of active free radicals, and improved the degradation efficiency of pollutants. The configuration and optical properties of the material were also determined. The effects of common ions and water environment on the photocatalytic degradation of CIP were also studied. The CIP possible degradation pathways were proposed on the basis of the identified intermediates by LC–MS.

2. Results and Discussion

2.1. Characterization of the Prepared Samples

The crystalline structure of the synthesized photocatalysts was measured by XRD, and the results are shown in Figure 1. The diffraction peaks of BiVO₄ at $2\theta = 15.1^\circ, 19.0^\circ, 28.9^\circ, 30.5^\circ, 34.5^\circ, 39.8^\circ, 42.5^\circ, 47.3^\circ, 50.3^\circ$, and 53.2° can correspond to the (020), (011), (−121), (040), (200), (211), (051), (042), (202), and (−161) planes of monoclinic scheelite type BiVO₄ (JCPDS No.14-0688) [30]. The diffraction peaks of BiVO₄ at $2\theta = 24.2^\circ, 32.6^\circ$, and 39.5° can be agreement with the (200), (112), and (301) planes of tetragonal zircon type BiVO₄ (JCPDS No: 14-0133) [31]. The position of diffraction peaks of Bi/BiVO₄ treated with NaBH₄ was basically the same as those of pristine BiVO₄, but its relative intensity decreased, thus indicating that its crystallinity was reduced. The $I(-121)/(040)$ of Bi/BiVO₄ first increased and then decreased with the increase in NaBH₄, thereby indicating that more (040) crystal planes were exposed, and the intensity of 0.3Bi-BVO (Bi/BiVO₄ prepared under NaBH₄ concentration of 0.30 g/L, see synthesis of photocatalyst for details) was the largest. According to previous reports [32], the (040) crystal plane can provide more active sites, which is conducive to the photocatalytic degradation of pollutants. In addition, no diffraction peak of Bi was observed, which is maybe due to little formation detected [33]. The concentration of NaBH₄ was increased to 4.00 g/L to clearly confirm the formation of metallic Bi. The XRD characterization of the obtained sample (4 Bi-BVO) is shown in Figure S1. The diffraction peak of $2\theta = 27.2^\circ$, which belongs to the (012) crystal plane of metallic Bi (JCPDS No.44-1246), could be found [34,35].

The characteristics of the synthesized sample's appearance were investigated via FESEM. In Figure 2a, the pristine BiVO₄ had an irregular rod-like structure. After the reduction by NaBH₄, the morphology did not change; however, small particles appeared on part of the BiVO₄ surface (Figure 2b).

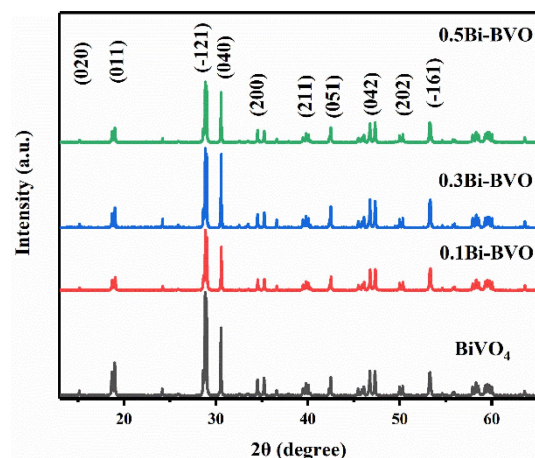


Figure 1. XRD patterns of BiVO_4 and Bi/BiVO_4 samples.

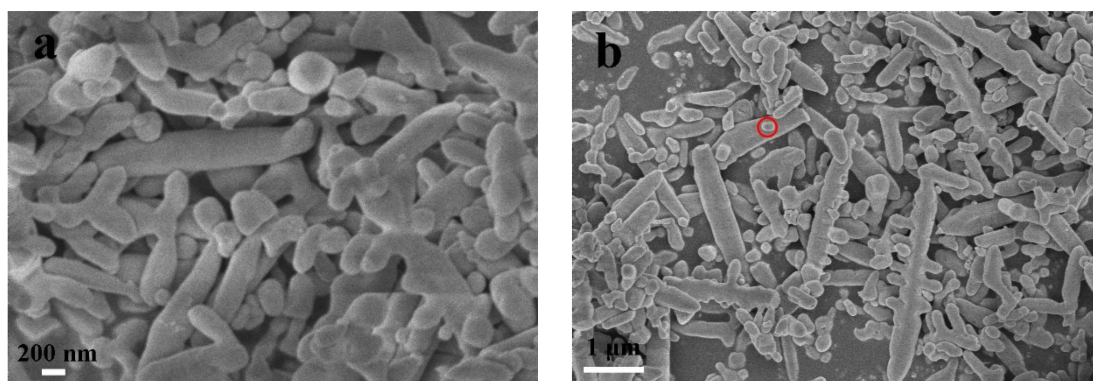


Figure 2. FESEM images of (a) BiVO_4 and (b) 0.3Bi-BVO.

XPS was performed to identify the surface element chemical status of the samples, and the results are shown in Figure 3. In Figure 3a, BiVO_4 and 0.3Bi-BVO identified the presence of Bi, V, O, and C elements. The V 2p fine spectrum of BiVO_4 and 0.3Bi-BVO displays two peaks at 524.8 and 517.2 eV, corresponding to V 2p_{1/2} and V 2p_{3/2} of the V^{5+} species, respectively (Figure 3b). Two peaks located at approximately 164.9 and 159.6 eV have been assigned to the spin-orbit coupling of Bi 4f_{5/2} and Bi 4f_{7/2} for the typical characteristics of Bi^{3+} ions, respectively. In comparison with the BiVO_4 , the Bi 4f binding energies of the 0.3Bi-BVO shift to the low binding energy side by approximately 0.2 eV (Figure 3c). The peaks located at 157.9 and 163.3 eV could be attributed to metallic Bi [27]. According to the semi-quantitative XPS, the atomic ratio of Bi 4f in BiVO_4 is 8.80%, and that of 0.3Bi-BVO is 9.25%; accordingly, Bi is generated. In Figure 3d, the bands centered at 530.3 and 531.5 eV were assigned to the lattice oxygen and the adsorbed oxygen [36], respectively. In comparison with the BiVO_4 , the O 1s binding energies of the 0.3Bi-BVO is negatively shifted. In addition, the peak area of the adsorbed oxygen becomes larger, which may be due to the existence of metallic Bi, which adsorbs more oxygen [37]. These results showed that the electron densities of Bi and O on the surface of the 0.3Bi-BVO are slightly higher than those on the BiVO_4 , which can be attributed to the transfer of electrons from metallic Bi to BiVO_4 [38]. The work function of Bi is ~4.22 eV [39]. The work function of BiVO_4 is generally greater than 4.22 eV [40–42]. Thus, the electron transfer from metallic Bi to BiVO_4 is theoretically feasible.

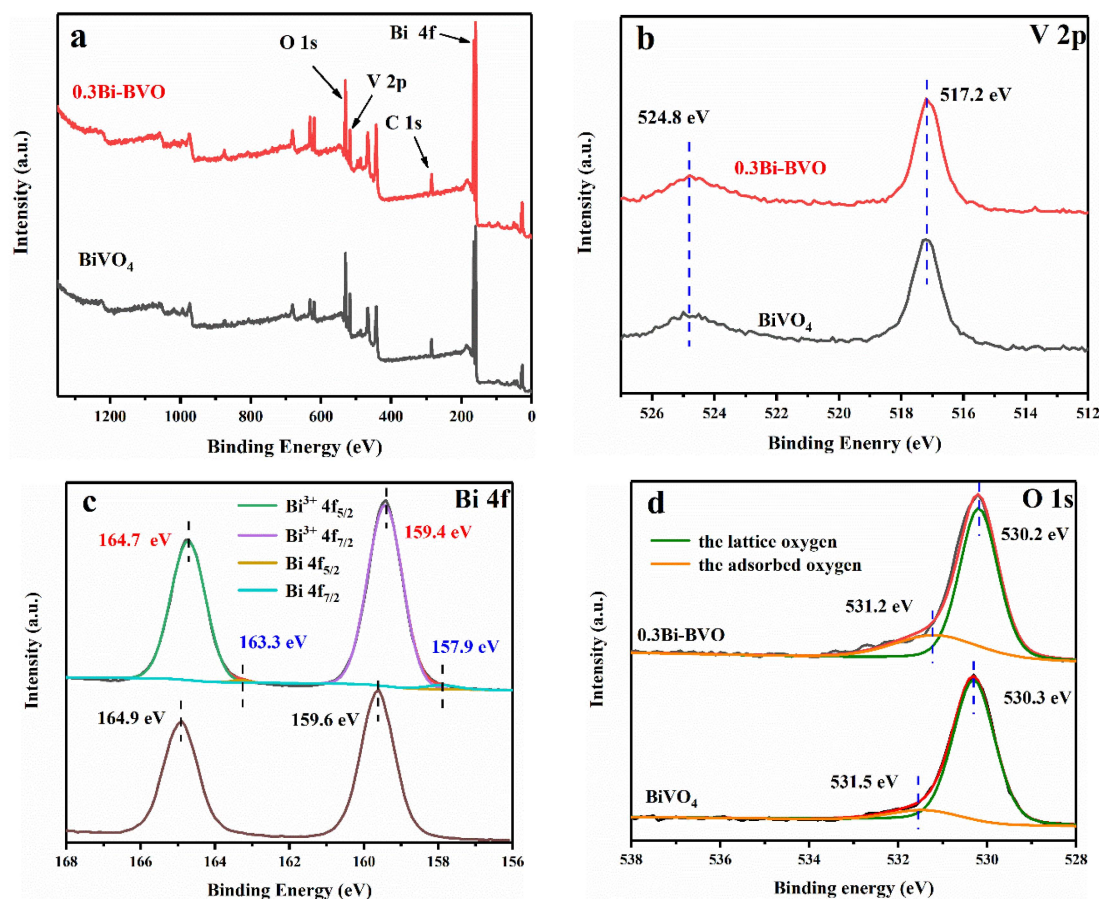


Figure 3. XPS spectra of 0.3Bi-BVO substances: (a) survey spectra, (b) V 2p spectra, (c) Bi 4f spectra, and (d) O 1s spectra.

The UV-vis diffuse reflectance spectroscopy (UV-vis DRS) of the samples was measured to explore their optical absorption properties (Figure 4a). The absorption edge of BiVO₄ and 0.3Bi-BVO is approximately 520 nm. However, the light absorption potential of 0.3Bi-BVO is slightly higher than that of BiVO₄, which should be due to the introduction of Bi [43]. The forbidden band width of BiVO₄ was determined to be 2.53 eV from the plots of $(\alpha h\nu)^2$ versus the energy of absorbed light (Figure 4b) [44]. The energy bands of pristine BiVO₄ were calculated using following equations:

$$E_{VB} = X - E_e + 0.5E_g, \quad (1)$$

$$E_{CB} = E_{VB} - E_g, \quad (2)$$

where E_{VB} and E_{CB} are the band edge potentials of the valence band (VB) and conduction band (CB), respectively; X is the absolute electronegativity of the materials, where X of BiVO₄ is 6.15 eV [45]; E_e is the energy of electrons on the hydrogen scale (~4.50 eV); and E_g is the band gap of the semiconductor in electron volts. The calculated E_{VB} and E_{CB} are 2.92 and 0.39 eV, respectively.

2.2. Photocatalytic Activity

The photocatalytic activity of the substances was evaluated via CIP degradation. In Figure 5, the control experiment indicated that little CIP degraded under visible light irradiation without the photocatalyst addition. The adsorption effect of the material on CIP is approximately 5% in the dark. Only 54% of the CIP was degraded within 30 min in the presence of pristine BiVO₄. The degradation of Bi/BiVO₄ samples was higher than that of BiVO₄. In addition, 0.3Bi-BVO displayed the most optimum photocatalytic activity, which had a degradation effect of 74% for CIP. Table 1 shows the pseudo-first-order kinetics of

the degradation of CIP, 0.3Bi-BVO exhibited the highest k value among those substances, which was approximately 1.82 times higher than that of BiVO_4 .

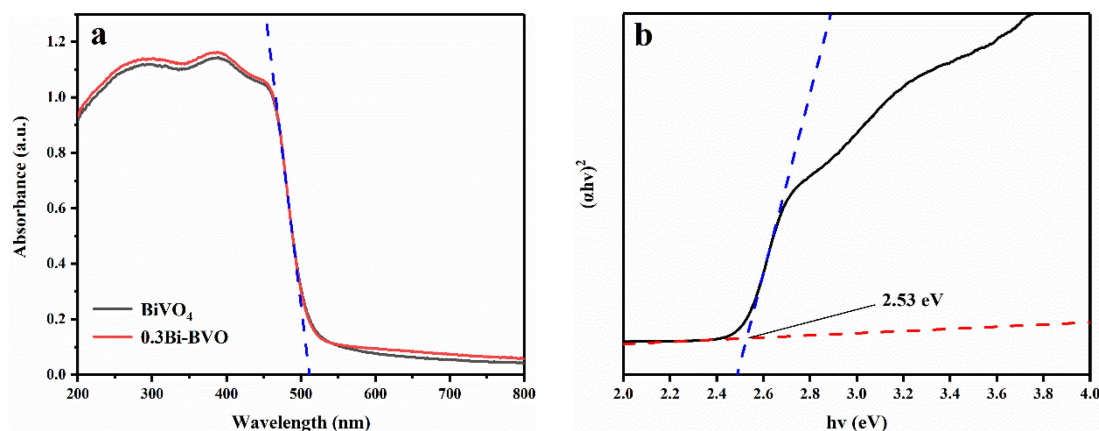


Figure 4. (a) UV-vis DRS of BiVO_4 and 0.3Bi-BVO and (b) plots of $(\alpha h\nu)^2$ versus $h\nu$ for BiVO_4 .

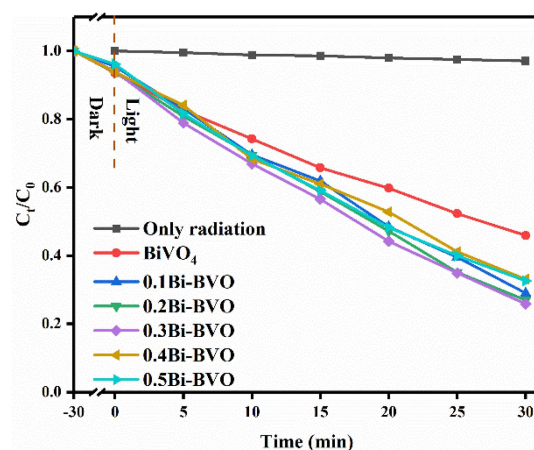


Figure 5. Photocatalytic degradation of ciprofloxacin (CIP) (reaction volume: 100 mL, initial CIP concentration: 10 mg/L, catalyst dose: 0.1 g, and temperature: 20 °C).

Table 1. Rate constant (k), and R^2 values for the degradation of ciprofloxacin.

Samples	k (min^{-1})	R^2
None	0.0010	0.9951
BiVO_4	0.0233	0.9985
0.1Bi-BVO	0.0387	0.9799
0.2Bi-BVO	0.0414	0.9794
0.3Bi-BVO	0.0423	0.9869
0.4Bi-BVO	0.0344	0.9855
0.5Bi-BVO	0.0360	0.9975

The stable performance of a photocatalyst is critical to its application. The cycling experiments measuring the degradation of CIP are performed to verify the stability and reusability of 0.3Bi-BVO. In Figure 6a, the degradation efficiency of CIP is reduced by approximately 4% after four cycles. The structure of the 0.3Bi-BVO used in the experiment is also investigated by XRD (Figure 6b). The intensity of (040) crystal planes of the used 0.3Bi-BVO is reduced compared with fresh 0.3Bi-BVO, which slightly affects the degradation of CIP.

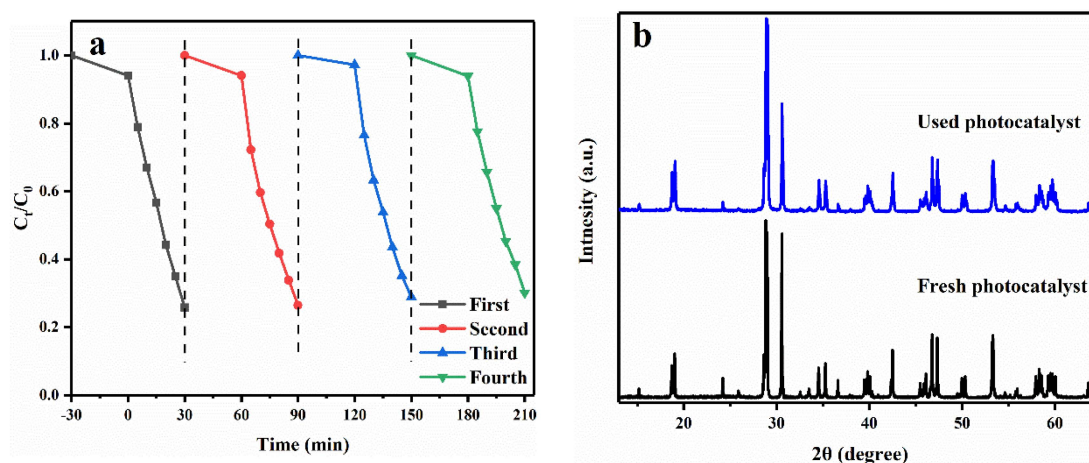


Figure 6. (a) Cyclic photocatalytic degradation of CIP in the presence of 0.3Bi-BVO (reaction volume: 100 mL, initial CIP concentration: 10 mg/L, catalyst dose: 0.1 g, and temperature: 20 °C) and (b) XRD patterns of the used photocatalyst and fresh photocatalyst.

Once released into the environment, the photocatalytic performance of a photocatalyst is closely associated with the other substances of surface water. First, the influence of other ions in the environment on the photocatalytic performance of the material must be considered. The influence of NaNO_3 , Na_2SO_4 , NaCl , and NaHCO_3 on the photocatalytic degradation of CIP was studied. Figure 7a shows the effects of CIP degradation in the existence of inorganic anions with a concentration of 10 mmol/L. The presence of NO_3^- and SO_4^{2-} did not inhibit the photocatalytic degradation of CIP. However, the removal percentages of CIP in the presence of HCO_3^- and Cl^- are 62% and 67%, respectively. HCO_3^- and Cl^- can be used as a trap to consume active free radicals generated on the surface of the catalyst, thereby affecting the degradation efficiency of CIP [46]. In addition, the degradation of CIP at different concentrations of humic acid (HA) had been studied. Figure S2 shows that the CIP degradation efficiency decreased from 74% to 63% with increasing HA concentration. This decrease may be attributed to HA, which can consume some active free radicals. Although the presence of HA has a certain negative effect on the photocatalytic degradation, overall, 0.3Bi-BVO still shows selectivity for CIP degradation. The effects of surface water on CIP degradation were studied to verify the feasibility of 0.3Bi-BVO to degrade CIP in the natural environment. In Figure 7b, although the degradation efficiency of the material is reduced in surface water, it can also achieve a certain degree of degradation of CIP.

2.3. Photocatalytic Mechanism

Free radical quenching tests were carried out to verify the main active free radicals in the degradation system of CIP. Isopropanol (IPA, 10 mmol/L), ascorbic acid (VC, 1 mmol/L) [47], and EDTA-2Na (1 mmol/L) were used for scavenging the hydroxyl radicals ($\cdot\text{OH}$), superoxide anion radicals ($\cdot\text{O}_2^-$), and h^+ reactive species, respectively. In Figure 8a, the removal percentages of CIP reduced from 74% to 69%, 20%, and 55% in the presence of IPA, VC, and EDTA-2Na, respectively. N_2 was also used to remove O_2 in the solution and hinder the generation of $\cdot\text{O}_2^-$ to further determine the role of $\cdot\text{O}_2^-$ [48], and the removal percentages of CIP was reduced to 5%. The results indicate that $\cdot\text{O}_2^-$ and h^+ play a major role in the photocatalytic system. ESR spin-trap with 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) in ethanol dispersion was used to prove the $\cdot\text{O}_2^-$ generation. In Figure 8b, pristine BiVO_4 and 0.3Bi-BVO had no characteristic peak under the dark conditions. By contrast, the characteristic peak of DMPO- $\cdot\text{O}_2^-$ appeared after 10 min of xenon lamp illumination, and the intensity of 0.3Bi-BVO was higher than that of BiVO_4 . Theoretically, the E_{CB} of BiVO_4 (+0.39 eV) is higher than the potential required for the formation of $\cdot\text{O}_2^-$ ($\text{O}_2/\cdot\text{O}_2^- = -0.046$ eV vs. NHE) [49], and $\cdot\text{O}_2^-$ cannot be generated. However, the oxygen vacancies (OVs) of BiVO_4 can activate O_2 and generate $\cdot\text{O}_2^-$ [50].

In addition, the presence of Bi could capture O_2 and improve the separation efficiency of photo-generated charges [29]. Therefore, 0.3Bi-BVO generates more $\cdot O_2^-$.

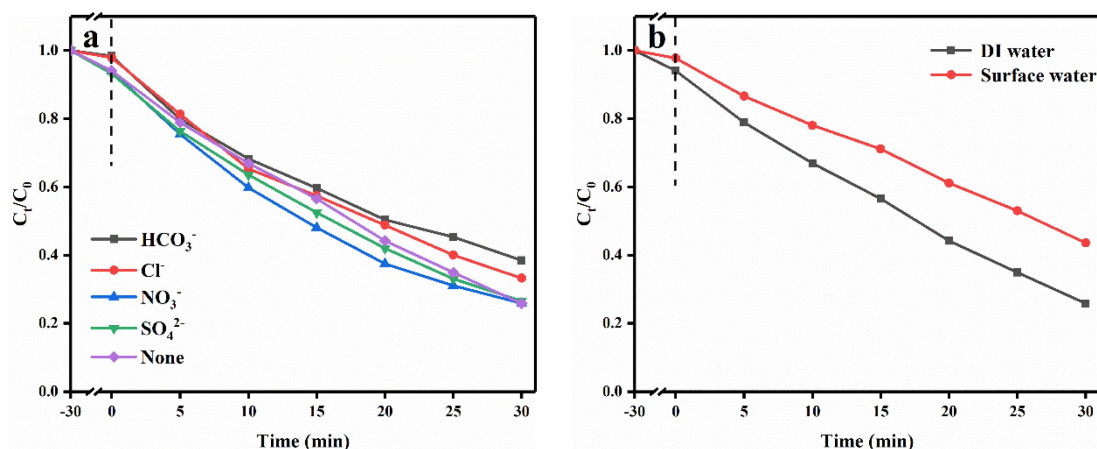


Figure 7. (a) Effect of different anions and (b) water on the degradation of CIP in the presence of 0.3Bi-BVO (reaction volume: 100 mL, initial CIP concentration: 10 mg/L, catalyst dose: 0.1 g, and temperature: 20 °C).

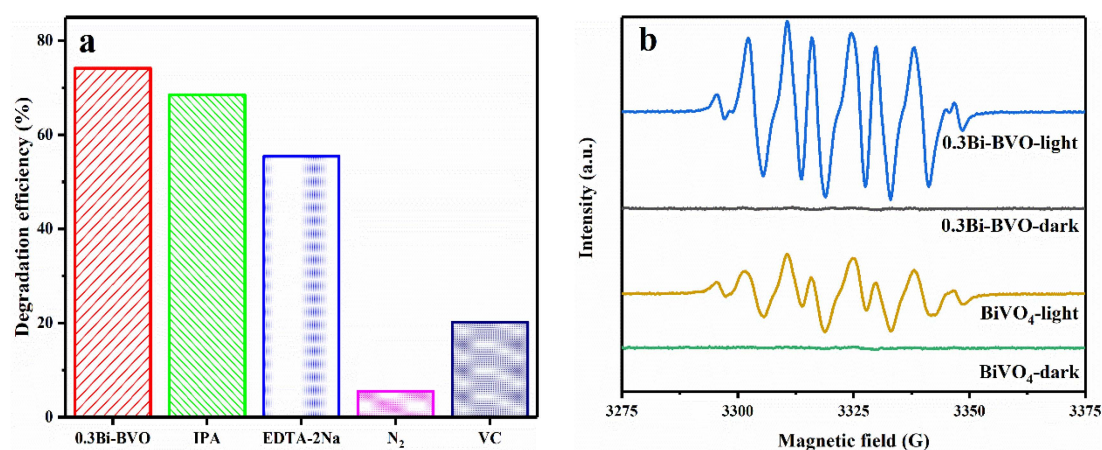


Figure 8. (a) Effect of different trapping agents on the photocatalytic degradation of CIP and (b) ESR spectra of DMPO- $\cdot O_2^-$ in the dark and under light irradiation.

PL spectra were employed to verify the photoinduced charge recombination and electron migration. In Figure 9a, the fluorescence spectrum of each sample had three relatively obvious peaks at the excitation wavelength of 295 nm. The emission at 534 nm corresponds to the radiation energy from the energy band transition of the sample. The emission peak at 425–452 and 600–620 nm may be related to the surface defect of the material [51]. The weaker the PL intensity, the lower the recombination rate of the photo-generated electron–hole pairs. The emission intensity of the 0.3Bi-BVO is lower than that of the pristine BiVO₄, which may be due to the existence of Bi inhibiting the recombination of the photogenerated charges. The photocurrent responses of the samples are depicted in Figure 9b. Bi/BiVO₄ exhibit a greatly enhanced photocurrent intensity compared with pristine BiVO₄ due to the presence of the metallic Bi, where 0.3Bi-BVO > 0.1Bi-BVO > 0.5Bi-BVO > BiVO₄, which is consistent with the result from the photocatalytic degradation of CIP. The above-mentioned results indicate that 0.3Bi-BVO has a better photo-generated charge separation efficiency.

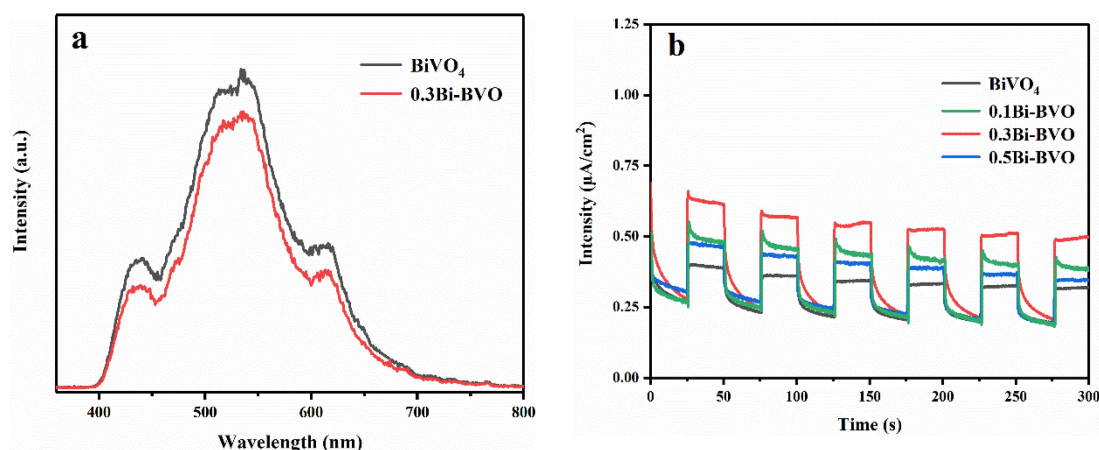


Figure 9. (a) PL spectra and (b) photocurrent responses of BiVO_4 and Bi/BiVO_4 .

The main intermediates were identified on the basis of LC–MS to understand the possible degradation pathways. Six intermediates are summarized in Table S1 and Supplementary Materials. Figure 10 shows the proposed photocatalytic degradation pathways of CIP on 0.3Bi-BVO. Path 1: $\cdot\text{O}_2^-$ attacked the piperazine side chain to form oxidative intermediate P1 ($m/z = 362$). Subsequently, intermediate P2 ($m/z = 334$) and intermediate P3 ($m/z = 306$) were derived from the loss of the $-\text{C}=\text{O}$ group of intermediate P1. Intermediate P3 could be further oxidized to intermediate P4 ($m/z = 291$). Intermediate P4 eliminated the $-\text{C}=\text{O}$ group and changed to intermediate P5 ($m/z = 263$) [52–54]. Path 2: Under the attack of h^+ , the quinolone ring of CIP decarboxylated to form intermediate P6 ($m/z = 288$) [55]. Path 3: h^+ attacked the piperazine ring to generate intermediate P3 [56].

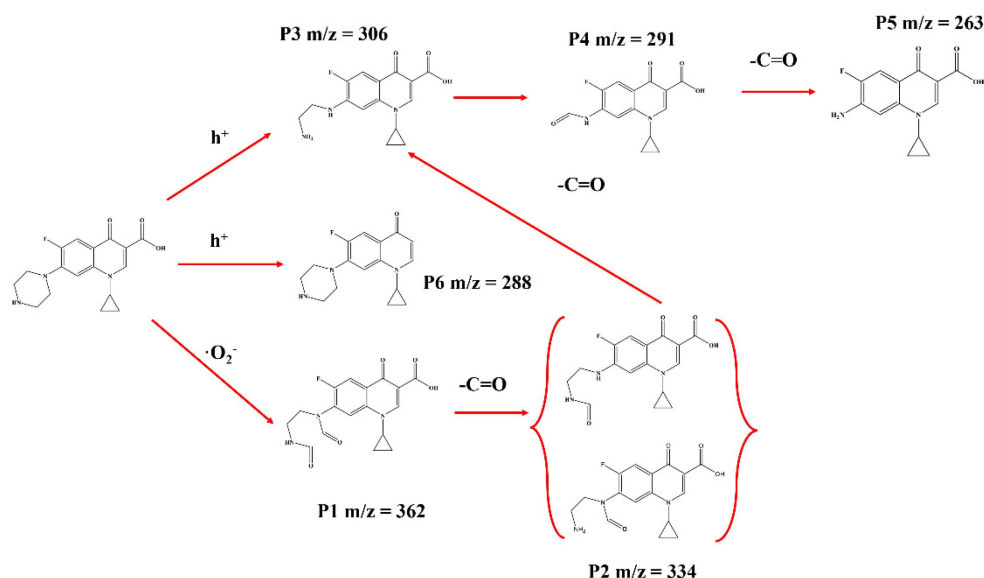
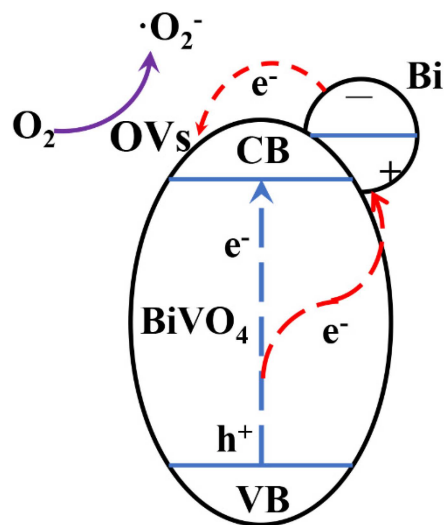


Figure 10. Possible degradation pathways of CIP on 0.3Bi-BVO.

On the basis of the active species trapping experiments, the ESR spin-trap, and the analysis of band edge position mentioned above, the reactive mechanism of great photocatalytic efficiency for 0.3Bi-BVO can be proposed. In Scheme 1, when visible light is irradiated to the substance, BiVO_4 generates photogenerated holes and photogenerated electrons, and Bi produces carriers due to the LSPR effect. Given that the E_{CB} (+0.39 eV) of BiVO_4 is lower than the Fermi level of metallic Bi (−0.17 eV) [57], the electrons of Bi can be transferred to BiVO_4 . Then, the Ovs of BiVO_4 can trap the electrons and make them react with O_2 to reduce to $\cdot\text{O}_2^-$. The positively charged Bi attracts the electrons generated

by BiVO_4 and returns to its original state [58]. This process can improve the separation efficiency of the photogenerated carriers of BiVO_4 .



Scheme 1. The possible mechanism for photocatalytic reactions happened on 0.3Bi-BVO.

3. Conclusions

In summary, a Bi/ BiVO_4 substance was successfully prepared by a NaBH_4 reduction method. The structure, morphology, composition, and photoelectric performance of the material were studied. 0.3Bi-BVO showed a better photocatalytic performance in the degradation of CIP. Active species trapping experiments confirmed that $\cdot\text{O}_2^-$ and h^+ were the main active groups in the photocatalytic degradation of CIP. The existence of Bi can increase the separation rate of the photo-generated charges and the generation of $\cdot\text{O}_2^-$, thereby improving the degradation efficiency of CIP. In addition, 0.3Bi-BVO had great stable performance and relatively great photocatalytic activity in natural water. This study offers a new option for photocatalytic degradation of residual drugs.

4. Materials and Methods

Materials: Bismuth chloride (BiCl_3) was obtained from Tianjin Kemiou Company, Tianjin, China. Ammonium vanadate (NH_4VO_3) was purchased from Xilong Chemical Company, Guangdong, China. Ethanolamine ($\text{C}_2\text{H}_7\text{NO}$) was purchased from Aladdin Industrial Corporation, Shanghai, China. CIP was procured from Shanghai Macklin Biochemical Co., Shanghai, China. NaBH_4 was obtained from Tianjin Damao Company, Tianjin, China. Deionized water was used throughout the experiment.

4.1. Synthesis of Photocatalyst

4.1.1. Synthesis of BiVO_4

BiVO_4 was synthesized according to a reported method [59]. First, 0.632 g of BiCl_3 was dispersed in 200 mL of deionized water and stirred to form a white dispersion. Second, 0.236 g of NH_4VO_3 was slowly added into the above white solution and magnetically stirred for 30 min, observing a color change from white to yellow. Afterward, 1.2 mL of $\text{C}_2\text{H}_7\text{NO}$ (1 mol/L) was added into the above-mentioned solution and sonicated for 30 min to ensure uniform dispersion, observing a color change from yellow to reddish brown. The resulting solution was transferred into a 100 mL Teflon-lined autoclave and heated at 160°C for 12 h. Finally, the resulting sediment after centrifugation was washed with ethanol and deionized water several times. The obtained substance was kept dried at 60°C in a drying oven for 12 h to obtain BiVO_4 .

4.1.2. Synthesis of Bi/BiVO₄

Bi/BiVO₄ was synthesized by using a NaBH₄ reduction method [57]. First, 0.40 g of BiVO₄ was dispersed in 60 mL of deionized water and ultrasonically dispersed for 30 min. Second, 20 mL of NaBH₄ solution of different concentrations was slowly added into the above solution and vigorously stirred for 1 h. Finally, the resulting sediment was washed with ethanol and deionized water several times and dried at 60 °C overnight to obtain Bi/BiVO₄. The concentrations of NaBH₄ were 0.10, 0.20, 0.30, 0.40, and 0.50 g/L, respectively. The obtained Bi/BiVO₄ substances were sequentially denoted as 0.1Bi-BVO, 0.2Bi-BVO, 0.3Bi-BVO, 0.4Bi-BVO, and 0.5Bi-BVO.

4.2. Characterization

The X-ray diffraction (XRD) patterns were measured with an X-ray diffractometer (Smart LAB SE, Rigaku, Tokyo, Japan) with Cu-K α radiation. A field emission scanning electron microscope (FESEM) and energy dispersive spectrometer (EDS) were performed on a ZEISS Gemini 500 (ZEISS, Jena, Germany). X-ray photoelectron spectroscopy (XPS) was performed on a Thermo ESCALAB 250Xi spectrometer (East Grinstead, UK). The binding energy data were calibrated with the C 1s peak at 284.8 eV. Ultraviolet–visible (UV-vis) spectroscopy was recorded with a UV-3600 Plus (Shimadzu, Kyoto, Japan) in the wavelength range of 200–800 nm. Photoluminescence (PL) spectroscopy was performed with a FLS980 spectrometer (Edinburgh, UK) by using the 295 nm line of a 450 W xenon lamp as the excitation source at room temperature, an R928P PMT as detector, and the scan slit and fixed/offset slit are 8 and 2 nm, respectively. Electron spin-resonance (ESR) spectroscopy was conducted with a Bruker A300 (Bruker, Karlsruhe, Germany) under irradiation with a 300 W xenon lamp.

Photocurrent measurements were performed in a three electrode quartz cells with 0.1 M Na₂SO₄ electrolyte solution by using a CHI 660E electrochemical workstation (Chenhua Instruments, Shanghai, China). Indium tin oxide (ITO) glass coated with the photocatalysts, a Pt electrode, and an Ag/AgCl electrode were used as the working electrode, auxiliary electrode, and reference electrode. The simulated optical source was a xenon lamp (300 W) with a cutoff filter. The working electrode was prepared as follows: 10 mg as-synthesized samples were mixed with 0.9 mL ethanol and 0.1 mL of Nafion solution and ultrasonically dispersed for 1 h to obtain the mixed solution. Then, 0.3 mL of mixture was dropwise-added to a 2 cm $\times$ 2 cm ITO glass. Finally, the prepared working electrode was dried at 50 °C for 6 h.

4.3. Photocatalytic Degradation Experiments

The photocatalytic performances of the fabricated photocatalysts were evaluated on the basis of CIP. Visible-light photocatalytic degradation was performed by using a solar simulator (300 W xenon lamp, PLS-SXE300, Beijing Perfectlight Technology Co., Ltd., China) as the light source, which was equipped with a UV filter ($\lambda > 400$ nm). First, 0.10 g of photocatalyst was dispersed in 100 mL of 10 mg/L CIP solution and magnetically stirred for 30 min in the dark to ensure the adsorption–desorption equilibrium. Next, the solution was illuminated with light in a photocatalytic reactor. Samples were taken every 5 min and filtered through a Millipore filter (pore size of 0.45 μ m) to remove the photocatalyst. The concentration of CIP was determined via HPLC (LC-20A, Shimadzu, Kyoto, Japan) with a Hypersil GOLD C18 (4.6 $\times$ 250 mm, 5 μ m) and UV–vis detector at 277 nm. The mobile phase was composed of water (0.5% [*v/v*] formic acid as an additive) and methanol (65:35, *v/v*). The flow rate was 0.9 mL/min. The column temperature was maintained at 35 °C.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/catal11040489/s1>, Figure S1: XRD patterns of 4 Bi-BVO sample, Figure S2: Effect of humic acid on the photocatalytic degradation of CIP, Table S1: Information on intermediates in the CIP photocatalytic process, and mass spectrum of the intermediates.

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References

- Salma, A.; Thoroe-Boveleth, S.; Schmidt, T.C.; Tuerk, J. Dependence of transformation product formation on pH during photolytic and photocatalytic degradation of ciprofloxacin. *J. Hazard. Mater.* **2016**, *313*, 49–59. [\[CrossRef\]](#)
- Rodriguez-Mozaz, S.; Chamorro, S.; Marti, E.; Huerta, B.; Gros, M.; Sánchez-Melsió, A.; Borrego, C.M.; Barceló, D.; Balcázar, J.L. Occurrence of antibiotics and antibiotic resistance genes in hospital and urban wastewaters and their impact on the receiving river. *Water Res.* **2015**, *69*, 234–242. [\[CrossRef\]](#) [\[PubMed\]](#)
- Mai, D.T.; Stuckey, D.C.; Oh, S. Effect of ciprofloxacin on methane production and anaerobic microbial community. *Bioresour. Technol.* **2018**, *261*, 240–248. [\[CrossRef\]](#) [\[PubMed\]](#)
- Rakshit, S.; Sarkar, D.; Elzinga, E.J.; Punamiya, P.; Datta, R. Mechanisms of ciprofloxacin removal by nano-sized magnetite. *J. Hazard. Mater.* **2013**, *246–247*, 221–226. [\[CrossRef\]](#) [\[PubMed\]](#)
- Chen, M.; Yao, J.; Huang, Y.; Gong, H.; Chu, W. Enhanced photocatalytic degradation of ciprofloxacin over Bi₂O₃/(BiO)₂CO₃ heterojunctions: Efficiency, kinetics, pathways, mechanisms and toxicity evaluation. *Chem. Eng. J.* **2018**, *334*, 453–461. [\[CrossRef\]](#)
- Berendonk, T.U.; Manaia, C.M.; Merlin, C.; Fatta-Kassinos, D.; Cytryn, E.; Walsh, F.; Bürgmann, H.; Sørum, H.; Norström, M.; Pons, M.-N.; et al. Tackling antibiotic resistance: The environmental framework. *Nat. Rev. Microbiol.* **2015**, *13*, 310–317. [\[CrossRef\]](#) [\[PubMed\]](#)
- Eggen, T.; Asp, T.N.; Grave, K.; Hormazabal, V. Uptake and translocation of metformin, ciprofloxacin and narasin in forage- and crop plants. *Chemosphere* **2011**, *85*, 26–33. [\[CrossRef\]](#) [\[PubMed\]](#)
- Polesel, F.; Lehnberg, K.; Dott, W.; Trapp, S.; Thomas, K.V.; Plósz, B.G. Factors influencing sorption of ciprofloxacin onto activated sludge: Experimental assessment and modelling implications. *Chemosphere* **2015**, *119*, 105–111. [\[CrossRef\]](#)
- Eslami, A.; Amini, M.M.; Yazdanbakhsh, A.R.; Mohseni-Bandpei, A.; Safari, A.A.; Asadi, A. N,S co-doped TiO₂ nanoparticles and nanosheets in simulated solar light for photocatalytic degradation of non-steroidal anti-inflammatory drugs in water: A comparative study. *J. Chem. Technol. Biotechnol.* **2016**, *91*, 2693–2704. [\[CrossRef\]](#)
- Kaur, A.; Kansal, S.K. Bi₂WO₆ nanocuboids: An efficient visible light active photocatalyst for the degradation of levofloxacin drug in aqueous phase. *Chem. Eng. J.* **2016**, *302*, 194–203. [\[CrossRef\]](#)
- Sood, S.; Mehta, S.K.; Sinha, A.S.K.; Kansal, S.K. Bi₂O₃/TiO₂ heterostructures: Synthesis, characterization and their application in solar light mediated photocatalyzed degradation of an antibiotic, ofloxacin. *Chem. Eng. J.* **2016**, *290*, 45–52. [\[CrossRef\]](#)
- Gu, S.; Li, W.; Wang, F.; Wang, S.; Zhou, H.; Li, H. Synthesis of buckhorn-like BiVO₄ with a shell of CeO_x nanodots: Effect of heterojunction structure on the enhancement of photocatalytic activity. *Appl. Catal. B-Environ.* **2015**, *170–171*, 186–194. [\[CrossRef\]](#)
- Palaniselvam, T.; Shi, L.; Mettela, G.; Anjum, D.H.; Li, R.; Katuri, K.P.; Saikaly, P.E.; Wang, P. Vastly Enhanced BiVO₄ Photocatalytic OER Performance by NiCoO₂ as Cocatalyst. *Adv. Mater. Interfaces* **2017**, *4*, 1700540. [\[CrossRef\]](#)
- Deng, Y.; Tang, L.; Feng, C.; Zeng, G.; Wang, J.; Zhou, Y.; Liu, Y.; Peng, B.; Feng, H. Construction of plasmonic Ag modified phosphorous-doped ultrathin g-C₃N₄ nanosheets/BiVO₄ photocatalyst with enhanced visible-near-infrared response ability for ciprofloxacin degradation. *J. Hazard. Mater.* **2018**, *344*, 758–769. [\[CrossRef\]](#) [\[PubMed\]](#)
- Pihosh, Y.; Turkevych, I.; Mawatari, K.; Uemura, J.; Kazoe, Y.; Kosar, S.; Makita, K.; Sugaya, T.; Matsui, T.; Fujita, D.; et al. Photocatalytic generation of hydrogen by core-shell WO₃/BiVO₄ nanorods with ultimate water splitting efficiency. *Sci. Rep.* **2015**, *5*, 11141. [\[CrossRef\]](#) [\[PubMed\]](#)
- Thalluri, S.M.; Hernández, S.; Bensaid, S.; Saracco, G.; Russo, N. Green-synthesized W- and Mo-doped BiVO₄ oriented along the {040} facet with enhanced activity for the sun-driven water oxidation. *Appl. Catal. B-Environ.* **2016**, *180*, 630–636. [\[CrossRef\]](#)
- Zhong, X.; He, H.; Yang, M.; Ke, G.; Zhao, Z.; Dong, F.; Wang, B.; Chen, Y.; Shi, X.; Zhou, Y. In³⁺-doped BiVO₄ photoanodes with passivated surface states for photoelectrochemical water oxidation. *J. Mater. Chem. A* **2018**, *6*, 10456–10465. [\[CrossRef\]](#)
- Jiang, D.; Xiao, P.; Shao, L.; Li, D.; Chen, M. RGO-Promoted All-Solid-State g-C₃N₄/BiVO₄ Z-Scheme Heterostructure with Enhanced Photocatalytic Activity toward the Degradation of Antibiotics. *Ind. Eng. Chem. Res.* **2017**, *56*, 8823–8832. [\[CrossRef\]](#)
- Bao, S.; Wu, Q.; Chang, S.; Tian, B.; Zhang, J. Z-scheme CdS–Au–BiVO₄ with enhanced photocatalytic activity for organic contaminant decomposition. *Catal. Sci. Technol.* **2017**, *7*, 124–132. [\[CrossRef\]](#)
- He, R.; Xu, D.; Cheng, B.; Yu, J.; Ho, W. Review on nanoscale Bi-based photocatalysts. *Nanoscale Horiz.* **2018**, *3*, 464–504. [\[CrossRef\]](#)

21. Liu, X.; Iocozzia, J.; Wang, Y.; Cui, X.; Chen, Y.; Zhao, S.; Li, Z.; Lin, Z. Noble metal–metal oxide nanohybrids with tailored nanostructures for efficient solar energy conversion, photocatalysis and environmental remediation. *Energy Environ. Sci.* **2017**, *10*, 402–434. [\[CrossRef\]](#)
22. Van, C.N.; Chang, W.S.; Chen, J.-W.; Tsai, K.-A.; Tzeng, W.-Y.; Lin, Y.-C.; Kuo, H.-H.; Liu, H.-J.; Chang, K.-D.; Chou, W.-C.; et al. Heteroepitaxial approach to explore charge dynamics across Au/BiVO₄ interface for photoactivity enhancement. *Nano Energy* **2015**, *15*, 625–633. [\[CrossRef\]](#)
23. Wu, J.; Wang, Y.; Liu, Z.; Yan, Y.; Zhu, Z. Preparation of noble metal Ag-modified BiVO₄ nanosheets and a study on the degradation performance of tetracyclines. *New J. Chem.* **2020**, *44*, 13815–13823. [\[CrossRef\]](#)
24. Dong, F.; Xiong, T.; Sun, Y.; Zhao, Z.; Zhou, Y.; Feng, X.; Wu, Z. A semimetal bismuth element as a direct plasmonic photocatalyst. *Chem. Commun.* **2014**, *50*, 10386–10389. [\[CrossRef\]](#)
25. Hu, J.; Xu, G.; Wang, J.; Lv, J.; Zhang, X.; Zheng, Z.; Xie, T.; Wu, Y. Photocatalytic properties of Bi/BiOCl heterojunctions synthesized using an in situ reduction method. *New J. Chem.* **2014**, *38*, 4913–4921. [\[CrossRef\]](#)
26. Dong, F.; Zhao, Z.; Sun, Y.; Zhang, Y.; Yan, S.; Wu, Z. An Advanced Semimetal-Organic Bi Spheres-g-C₃N₄ Nanohybrid with SPR-Enhanced Visible-Light Photocatalytic Performance for NO Purification. *Environ. Sci. Technol.* **2015**, *49*, 12432–12440. [\[CrossRef\]](#)
27. Wang, K.; Li, Y.; Zhang, G.; Li, J.; Wu, X. 0D Bi nanodots/2D Bi₃NbO₇ nanosheets heterojunctions for efficient visible light photocatalytic degradation of antibiotics: Enhanced molecular oxygen activation and mechanism insight. *Appl. Catal. B-Environ.* **2019**, *240*, 39–49. [\[CrossRef\]](#)
28. Wang, B.; Feng, W.; Zhang, L.; Zhang, Y.; Huang, X.; Fang, Z.; Liu, P. In situ construction of a novel Bi/CdS nanocomposite with enhanced visible light photocatalytic performance. *Appl. Catal. B-Environ.* **2017**, *206*, 510–519. [\[CrossRef\]](#)
29. Lai, M.; Zhao, J.; Chen, Q.; Feng, S.; Bai, Y.; Li, Y.; Wang, C. Photocatalytic toluene degradation over Bi-decorated TiO₂: Promoted O₂ supply to catalyst's surface by metallic Bi. *Catal. Today* **2019**, *335*, 372–380. [\[CrossRef\]](#)
30. Pan, Q.; Yang, K.; Wang, G.; Li, D.; Sun, J.; Yang, B.; Zou, Z.; Hu, W.; Wen, K.; Yang, H. BiVO₄ nanocrystals with controllable oxygen vacancies induced by Zn-doping coupled with graphene quantum dots for enhanced photoelectrochemical water splitting. *Chem. Eng. J.* **2019**, *372*, 399–407. [\[CrossRef\]](#)
31. Packiaraj, R.; Devendran, P.; Asath Bahadur, S.; Nallamuthu, N. Structural and electrochemical studies of Scheelite type BiVO₄ nanoparticles: Synthesis by simple hydrothermal method. *J. Mater. Sci. Mater. Electron.* **2018**, *29*, 13265–13276. [\[CrossRef\]](#)
32. Wang, D.; Jiang, H.; Zong, X.; Xu, Q.; Ma, Y.; Li, G.; Li, C. Crystal facet dependence of water oxidation on BiVO₄ sheets under visible light irradiation. *Chem. Eur. J.* **2011**, *17*, 1275–1282. [\[CrossRef\]](#) [\[PubMed\]](#)
33. Lv, J.; Zhang, J.; Liu, J.; Li, Z.; Dai, K.; Liang, C. Bi SPR-Promoted Z-Scheme Bi₂MoO₆/CdS-Diethylenetriamine Composite with Effectively Enhanced Visible Light Photocatalytic Hydrogen Evolution Activity and Stability. *ACS Sustain. Chem. Eng.* **2017**, *6*, 696–706. [\[CrossRef\]](#)
34. Tao, S.; Sun, S.; Zhao, T.; Cui, J.; Yang, M.; Yu, X.; Yang, Q.; Zhang, X.; Liang, S. One-pot construction of Ta-doped BiOCl/Bi heterostructures toward simultaneously promoting visible light harvesting and charge separation for highly enhanced photocatalytic activity. *Appl. Surf. Sci.* **2021**, *543*, 148798. [\[CrossRef\]](#)
35. Liu, Z.; Jin, S.; Cui, K.; Zhao, J.; Xie, S.; Li, J.; Xinghua, C. Cavity containing core-shell Bi@C nanowires toward high performance lithium ion batteries. *J. Alloy. Compd.* **2020**, *842*, 155796. [\[CrossRef\]](#)
36. Zhang, J.; Cui, H.; Wang, B.; Li, C.; Zhai, J.; Li, Q. Preparation and characterization of fly ash cenospheres supported CuO–BiVO₄ heterojunction composite. *Appl. Surf. Sci.* **2014**, *300*, 51–57. [\[CrossRef\]](#)
37. Regmi, C.; Kshetri, Y.K.; Kim, T.-H.; Pandey, R.P.; Ray, S.K.; Lee, S.W. Fabrication of Ni-doped BiVO₄ semiconductors with enhanced visible-light photocatalytic performances for wastewater treatment. *Appl. Surf. Sci.* **2017**, *413*, 253–265. [\[CrossRef\]](#)
38. Zhen, Y.; Yang, C.; Shen, H.; Xue, W.; Gu, C.; Feng, J.; Zhang, Y.; Fu, F.; Liang, Y. Photocatalytic performance and mechanism insights of a S-scheme g-C₃N₄/Bi₂MoO₆ heterostructure in phenol degradation and hydrogen evolution reactions under visible light. *Phys. Chem. Chem. Phys.* **2020**, *22*, 26278–26288. [\[CrossRef\]](#)
39. Xiao, J.; Yang, W.; Li, Q. Bi quantum dots on rutile TiO₂ as hole trapping centers for efficient photocatalytic bromate reduction under visible light illumination. *Appl. Catal. B-Environ.* **2017**, *218*, 111–118. [\[CrossRef\]](#)
40. Xie, Q.; He, W.; Liu, S.; Li, C.; Zhang, J.; Wong, P.K. Bifunctional S-scheme g-C₃N₄/Bi/BiVO₄ hybrid photocatalysts toward artificial carbon cycling. *Chin. J. Catal.* **2020**, *41*, 140–153. [\[CrossRef\]](#)
41. Liu, X.; Yuan, Y.; Liu, J.; Liu, B.; Chen, X.; Ding, J.; Han, X.; Deng, Y.; Zhong, C.; Hu, W. Utilizing solar energy to improve the oxygen evolution reaction kinetics in zinc-air battery. *Nat. Commun.* **2019**, *10*, 4767. [\[CrossRef\]](#)
42. Zhou, C.; Wang, S.; Zhao, Z.; Shi, Z.; Yan, S.; Zou, Z. A Facet-Dependent Schottky-Junction Electron Shuttle in a BiVO₄ {010}-Au-Cu₂O Z-Scheme Photocatalyst for Efficient Charge Separation. *Adv. Funct. Mater.* **2018**, *28*, 1801214. [\[CrossRef\]](#)
43. Gnayem, H.; Sasson, Y. Nanostructured 3D Sunflower-like Bismuth Doped BiOCl_xBr_{1-x} Solid Solutions with Enhanced Visible Light Photocatalytic Activity as a Remarkably Efficient Technology for Water Purification. *J. Phys. Chem. C* **2015**, *119*, 19201–19209. [\[CrossRef\]](#)
44. Makula, P.; Pacia, M.; Macyk, W. How to Correctly Determine the Band Gap Energy of Modified Semiconductor Photocatalysts Based on UV-Vis Spectra. *J. Phys. Chem. Lett.* **2018**, *9*, 6814–6817. [\[CrossRef\]](#)
45. Kumar, A.; Shalini, G.S.; Naushad, M.; Kumar, A.; Kalia, S.; Guo, C.; Mola, G.T. Facile hetero-assembly of superparamagnetic Fe₃O₄/BiVO₄ stacked on biochar for solar photo-degradation of methyl paraben and pesticide removal from soil. *J. Photochem. Photobiol. A-Chem.* **2017**, *337*, 118–131. [\[CrossRef\]](#)

46. Jiang, Y.; Zhang, M.; Xin, Y.; Chai, C.; Chen, Q. Construction of immobilized CuS/TiO₂ nanobelts heterojunction photocatalyst for photocatalytic degradation of enrofloxacin: Synthesis, characterization, influencing factors and mechanism insight. *J. Chem. Technol. Biotechnol.* **2019**, *94*, 2219–2228. [\[CrossRef\]](#)
47. Omrani, N.; Nezamzadeh-Ejhieh, A. A ternary Cu₂O/BiVO₄/WO₃ nano-composite: Scavenging agents and the mechanism pathways in the photodegradation of sulfasalazine. *J. Mol. Liq.* **2020**, *315*, 113701. [\[CrossRef\]](#)
48. Li, D.; Song, H.; Meng, X.; Shen, T.; Sun, J.; Han, W.; Wang, X. Effects of Particle Size on the Structure and Photocatalytic Performance by Alkali-Treated TiO₂. *Nanomaterials* **2020**, *10*, 546. [\[CrossRef\]](#)
49. Zhang, D.; Hao, J.; Wan, P.; Zhang, D.; Sun, Q.; Liu, Z.; Li, F.; Fang, H.; Wang, Y. Synergy of charge pre-separation and direct Z-scheme bridge in BiVO₄{0 4 0}/Ag₆Si₂O₇ photocatalyst boosting organic pollutant degradation. *Appl. Surf. Sci.* **2020**, *513*, 145832. [\[CrossRef\]](#)
50. Xu, J.; Bian, Z.; Xin, X.; Chen, A.; Wang, H. Size dependence of nanosheet BiVO₄ with oxygen vacancies and exposed {001} facets on the photodegradation of oxytetracycline. *Chem. Eng. J.* **2018**, *337*, 684–696. [\[CrossRef\]](#)
51. Arunachalam, M.; Jun Seo, Y.; Jeon, S.; Ahn, K.-S.; Soo Kim, C.; Hyung Kang, S. Colloidal metal Ag nanowire as an efficient co-catalyst for enhancing the solar water oxidation of fluorinated BiVO₄ photoelectrode. *Chem. Eng. J.* **2020**, *394*, 125016. [\[CrossRef\]](#)
52. Yu, M.; Liang, H.; Zhan, R.; Xu, L.; Niu, J. Sm-doped g-C₃N₄/Ti₃C₂ MXene heterojunction for visible-light photocatalytic degradation of ciprofloxacin. *Chin. Chem. Lett.* **2020**. [\[CrossRef\]](#)
53. Hu, K.; Li, R.; Ye, C.; Wang, A.; Wei, W.; Hu, D.; Qiu, R.; Yan, K. Facile synthesis of Z-scheme composite of TiO₂ nanorod/g-C₃N₄ nanosheet efficient for photocatalytic degradation of ciprofloxacin. *J. Clean Prod.* **2020**, *253*, 120055. [\[CrossRef\]](#)
54. Yu, H.; Huang, B.; Wang, H.; Yuan, X.; Jiang, L.; Wu, Z.; Zhang, J.; Zeng, G. Facile construction of novel direct solid-state Z-scheme AgI/BiOBr photocatalysts for highly effective removal of ciprofloxacin under visible light exposure: Mineralization efficiency and mechanisms. *J. Colloid Interface Sci.* **2018**, *522*, 82–94. [\[CrossRef\]](#) [\[PubMed\]](#)
55. Xu, J.; Li, X.; Niu, J.; Chen, M.; Yue, J. Synthesis of direct Z-Scheme Bi₃TaO₇/CdS composite photocatalysts with enhanced photocatalytic performance for ciprofloxacin degradation under visible light irradiation. *J. Alloy. Compd.* **2020**, *834*, 155061. [\[CrossRef\]](#)
56. Wang, F.; Feng, Y.; Chen, P.; Wang, Y.; Su, Y.; Zhang, Q.; Zeng, Y.; Xie, Z.; Liu, H.; Liu, Y.; et al. Photocatalytic degradation of fluoroquinolone antibiotics using ordered mesoporous g-C₃N₄ under simulated sunlight irradiation: Kinetics, mechanism, and antibacterial activity elimination. *Appl. Catal. B-Environ.* **2018**, *227*, 114–122. [\[CrossRef\]](#)
57. Sun, Y.; Zhao, Z.; Zhang, W.; Gao, C.; Zhang, Y.; Dong, F. Plasmonic Bi metal as cocatalyst and photocatalyst: The case of Bi/(BiO)₂CO₃ and Bi particles. *J. Colloid Interface Sci.* **2017**, *485*, 1–10. [\[CrossRef\]](#) [\[PubMed\]](#)
58. Jing, Q.; Feng, X.; Zhao, X.; Duan, Z.; Pan, J.; Chen, L.; Liu, Y. Bi/BiVO₄ Chainlike Hollow Microstructures: Synthesis, Characterization, and Application as Visible-Light-Active Photocatalysts. *ACS Appl. Nano Mater.* **2018**, *1*, 2653–2661. [\[CrossRef\]](#)
59. Xi, G.; Ye, J. Synthesis of bismuth vanadate nanoplates with exposed {001} facets and enhanced visible-light photocatalytic properties. *Chem. Commun.* **2010**, *46*, 1893–1895. [\[CrossRef\]](#)