

Article

Fabrication of Novel ZIF-8@BiVO₄ Composite with Enhanced Photocatalytic Performance

Yun-hui Si ^{1,†}, Ya-yun Li ^{1,*†}, Yu Xia ¹, Shao-ke Shang ¹, Xin-bo Xiong ^{1,*}, Xie-rong Zeng ¹ and Ji Zhou ²

¹ Shenzhen Key Laboratory of Special Functional Materials & Shenzhen Engineering Laboratory for Advance Technology of Ceramics, College of Materials Science and Engineering, Shenzhen University, Shenzhen 518060, China; 2161120218@email.szu.edu.cn (Y.-h.S.); 2172341411@email.szu.edu.cn (Y.X.); 2172341466@email.szu.edu.cn (S.-k.S.); zengxier@szu.edu.cn (X.-r.Z.)

² State Key Laboratory of New Ceramics and Fine Processing, School of Materials Science and Engineering, Tsinghua University, Beijing 100084, China; zhouji@tsinghua.edu.cn

* Correspondence: kittylis@szu.edu.cn (Y.-y.L.); xxbszdx@szu.edu.cn (X.-b.X.)

† These authors contributed equally to this paper.

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Abstract: In this work, a novel metal-organic framework (MOF) and BiVO₄ (BVO) composite photocatalyst was successfully synthesized by an in-situ growth method. The characterization of obtained samples was done by X-ray diffraction, scanning electron microscopy, energy dispersive spectroscopy, N₂ adsorption, and photoluminescence spectroscopy. The photocatalytic performance of ZIF-8@BiVO₄ composite was evaluated by the degradation of methylene blue (MB) under simulated visible light irradiation. Compared with the mixture of BVO and ZIF-8, the composite photocatalyst exhibited superior photodegradation efficiency, which could be attributed to the synergistic effect between BVO and ZIF-8. The reduced recombination of photogenerated electrons and holes was considered to be an important reason for the enhancement of photocatalytic performance. This design demonstrates a rational method to improve the photocatalytic performance by combining photocatalysts with MOFs.

Keywords: BiVO₄; MOFs; photocatalyst; visible light

1. Introduction

For a long time, human beings have been exploring how to effectively utilize the inexhaustible energy of the Sun and transform its light energy into electrical and chemical energy, which are research hot spots. Photocatalysis makes use of the light energy existing in the natural world to produce catalytic action, so that oxygen and water molecules are adsorbed on the photocatalyst itself, producing free radicals with strong oxidizing properties [1]. These free radicals can degrade almost all organic and some inorganic substances that are harmful to the environment, and do not cause waste of resources or additional pollution. In recent years, the discovery of visible light response photocatalysts has greatly increased the utilization efficiency of sunlight [2]. In addition to modifying the traditional photocatalytic material TiO₂ to achieve visible light response [3], numerous efforts have been directed toward the development of efficient visible light responsive photocatalytic materials such as BFO, BiVO₄ (BVO), and g-C₃N₄ [4–7]. BiVO₄ is a typical narrow band gap semiconductor oxide with excellent visible light catalytic performance and high photoelectric conversion efficiency. It has attracted extensive attention due to its good performance in photocatalytic water splitting and the degradation of organic pollutants [8–10]. Although BiVO₄ has high photocatalytic activity, the disadvantages of weak surface adsorption capacity and high recombination of photogenerated electrons and holes limit its

wide application in the industry. In order to improve the photocatalytic activity of BiVO_4 , many studies have been conducted on the modification of BiVO_4 . The common modification approaches include ion doping, composite materials, and the loading of noble metals [11–13].

Metal-organic frameworks (MOFs) are a kind of organic–inorganic hybrid nano-porous material comprised of organic ligands and metal ions or metal clusters. Compared with inorganic porous materials such as zeolite molecular sieve, MOFs have become one of the research hot spots of multifunctional materials because of their advantages of large specific surface area and controllable structure [14,15]. MOFs have more options for photocatalysis because of the large number of organic ligands and metal ions available, and the combination of organic ligands and metal ions is also flexible. Therefore, MOFs have potential applications in photocatalytic CO_2 reduction, organic synthesis, or water splitting to produce hydrogen and oxygen [16–18]. In addition, MOF materials have attracted extensive attention in wastewater treatment, and the development of novel MOF photocatalysts has become a research hotspot [19,20]. Zeolitic imidazolate frameworks (ZIFs) are a kind of MOF material with zeolite framework structure, combining the high stability of zeolite and the structural diversity of MOF materials [21]. As a representative material in ZIFs, ZIF-8 has good porosity and large specific surface area, and is widely used in the fields of catalysis [22], sensing [23], gas adsorption, and separation [24]. It is particularly interesting that MOFs can be used as co-catalysts in the photocatalytic process because of their large pore volume and high thermal stability [25]. In addition, a variety of functional groups and unsaturated metal atoms on organic ligands can be used as the catalytic activity centers.

So far, there are few reports on the combination of ZIF-8 with highly active photocatalyst. In this work, we successfully synthesized ZIF-8@BVO composite photocatalyst by an in-situ growth method. ZIF-8@BVO composite was characterized, and its photocatalytic performance was evaluated by the degradation of MB under visible light irradiation. The production of hydroxyl ($\cdot\text{OH}$) radicals was investigated using photoluminescence method with terephthalic acid (TA) as a probing molecule. In addition, the stability of the composite catalyst was verified by cyclic experiments. The possible mechanism of the improved photocatalytic performance was also proposed.

2. Experimental Section

2.1. Materials

All the chemicals, including bismuth nitrate pentahydrate ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$), ammonium vanadate (NH_4VO_3), sodium hydroxide (NaOH), sodium dodecylbenzenesulfonate ($\text{C}_{18}\text{H}_{29}\text{NaO}_3\text{S}$), zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), 2-methylimidazole ($\text{C}_4\text{H}_6\text{N}_2$), methanol (CH_4O), and methylene blue (MB) were purchased from Macklin Biochemical Co., Ltd., Shanghai, China. The chemicals were of analytical grade and used as received without further purification. Deionized water was used throughout this work.

2.2. Synthesis of BVO

BVO nanosheets were synthesized by a traditional hydrothermal method reported in the literature [26]. In a typical synthesis, 5 mmol $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ was dissolved in 10 mL nitric acid (4 M) solution. Meanwhile, equimolar NH_4VO_3 was added to 10 mL NaOH solution (2 M). Then, 0.25 g SDBS was added to both solutions. The above solutions were stirred for 30 min to ensure that the solutes were completely dissolved. After that, the two solutions were mixed to obtain a bright yellow mixture. The pH value of the mixture was adjusted to 7 by the addition of NaOH solution (2 M), and the mixture was kept stirring for 30 min. The mixture was transferred into a 50 mL Teflon-lined vessel followed by a hydrothermal process at 200 °C for 1.5 h. After the reaction, the autoclave was cooled to room temperature naturally. The final product was centrifuged and washed with deionized water several times, and dried at 80 °C for 10 h.

2.3. Synthesis of ZIF-8@BVO Composite

The preparation of ZIF-8@BVO composite was carried out through an in-situ growth method on the surface of BVO. In a typical synthesis, 1 g BVO nanosheets was dispersed in 100 mL methanol with the assistance of ultrasonication, 2.5 mmol $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was dissolved in the suspension, and 5 mmol 2-methylimidazole was dissolved in another 100 mL of methanol. The molar ratio of ZIF-8 to BVO was about 1:1.2, and it could be controlled by adjusting the amount of zinc nitrate. Subsequently, the two solutions were mixed and stirred for 1 h. The final product was collected by centrifugation and washed with methanol, then dried for 8 h in the fume hood. In comparison, pure ZIF-8 was synthesized following the same method without the addition of BVO [27].

2.4. Characterization

X-ray diffraction with $\text{Cu K}\alpha$ radiation (D8Advance, Bruker, Karlsruhe, Germany) was carried out to examine the phases of as-prepared samples. The morphology of samples was observed by scanning electron microscope (SU70, Hitachi, Tokyo, Japan). Energy dispersive spectroscopy (EDS) was used to investigate the chemical composition of the sample. The Brunauer–Emmett–Teller (BET) specific surface area of the samples was measured based on nitrogen adsorption isotherm (77 K) using a surface area analyzer (Micromeritics ASAP 2020, Shanghai, China).

2.5. Analysis of $\cdot\text{OH}$ Radical

The increased number of $\cdot\text{OH}$ radicals was investigated by PL method, and terephthalic acid (TA) was used as a probing molecule to analyze the production of hydroxyl radicals during the photocatalytic reaction. In the photocatalytic process, TA can be converted into a highly fluorescent molecule known as 2-hydroxyterephthalic acid (HTA) by chemical reaction with the active species $\cdot\text{OH}$ radicals in solution. The fluorescence intensity of TAOH is directly proportional to the amount of $\cdot\text{OH}$ [28]. In order to analyze the production of $\cdot\text{OH}$ radical, TA was dissolved in 1 mmol/L NaOH solution to make a 2.5×10^{-4} mol/L TA-NaOH solution. The mixed solution was added to a reactor containing 200 mg of the photocatalyst, and the suspension was stirred constantly under visible light irradiation for 100 min. The reaction solution was centrifuged to separate the photocatalyst and then used for PL measurement on a photoluminescence spectroscope (F-4500, Hitachi, Tokyo, Japan) with an excitation wavelength of 325 nm.

2.6. Photocatalytic Experiment

The photocatalytic behavior of as-prepared samples was evaluated by the degradation of methylene blue (MB) solution under visible light irradiation using a 300 W xenon lamp (cutoff filter, $\lambda > 420$ nm). In order to avoid any thermal effect, the temperature of the reaction vessel was maintained at 23–26 °C by circulating cooling water. In our photo-degradation experiments, 80 mL MB solution was used as target pollutant, and the initial concentration was 20 mg/L. MB solution was added to a reactor containing 20 mg of the photocatalyst, and the suspension was stirred for 30 min in the dark to reach adsorption equilibrium before visible light irradiation. In the process of photodegradation, 1 mL of solution was removed every 20 min and diluted in 4 mL of deionized water. The sampling solution was centrifuged to separate the photocatalyst from the solution. The concentration of MB solution was determined by measuring the absorbance at 663 nm via a UV–Vis spectrophotometer (Shimadzu, UV-2450, Kyoto, Japan). The photocatalytic degradation efficiency (η) was calculated based on the formula $\eta = (1 - C/C_0) \times 100\%$, where C and C_0 present the final and initial concentration of MB solution. In addition, the ZIF-8@BVO composite and the mixture of BVO and ZIF-8 were reused three times to verify the stability of the photocatalyst. In the cycling experiment, the photocatalyst was separated from the solution by centrifugation after the photocatalytic reaction. The collected samples were washed repeatedly with deionized water and ethanol to remove the dye molecules adsorbed on the surface, then placed in a vacuum oven at 80 °C for 12 h. In addition, in order to compensate for

the loss of catalyst during the cycle, the initial test was carried out using two identical photocatalysts under the same conditions.

3. Results and Discussion

3.1. Phase Structure and Morphology

Figure 1a shows the XRD patterns of ZIF-8@BVO composite and pure BVO. In respect of BVO, the diffraction peaks located at 18.98° , 28.94° , 30.58° , and 35.22° were in agreement with the (011), (121), (040), and (161) face of monoclinic structure BiVO_4 (JCPDS No. 014-0688). No other diffraction peak was detected, suggesting the high purity of as-prepared BVO. For ZIF-8@BVO composite, the weak diffraction peaks located at 7.46° , 10.42° , 12.80° , 16.43° , and 24.50° could be indexed to the (011), (002), (112), (013), and (233) crystal face of ZIF-8, and the remaining peaks belonged to the pure BVO. Remarkably, the coexistence of two phases of BVO and ZIF-8 indicated the successful preparation of ZIF-8@BVO composite. Moreover, the diffraction peaks of pure ZIF-8 were consistent with those of simulated sample, as shown in Figure 1b.

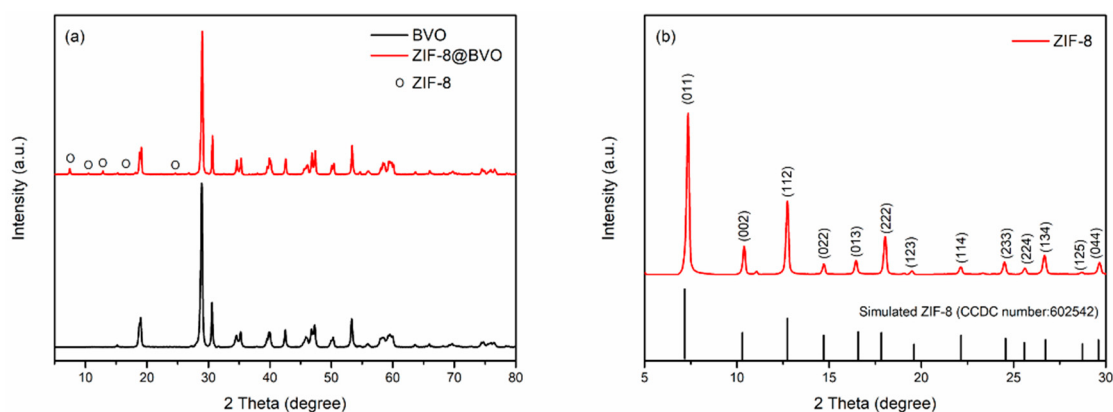


Figure 1. XRD pattern of (a) BiVO_4 (BVO) and ZIF-8@BVO, (b) ZIF-8. ZIF: zeolitic imidazolate framework; ZIF-8@BVO: ZIF-8–BVO composite photocatalyst.

The morphology images of as-prepared samples are shown in Figure 2a–c. As shown in Figure 2a, it is clear that the prepared BVO had a nanoplatelets structure with a thickness of 30–50 nm, and no nanoparticles were observed. It can be seen from Figure 2b that ZIF-8 was well-crystallized, showing a spherical structure with a particle size of about 50–80 nm. Figure 2c shows that ZIF-8 nanoparticles were uniformly dispersed on the surface of BVO. In addition, the EDS results showed that Bi, O, V, C, and Zn elements were uniformly distributed in the composite, proving that ZIF-8 was well-dispersed on the BVO surface (Figure 3).

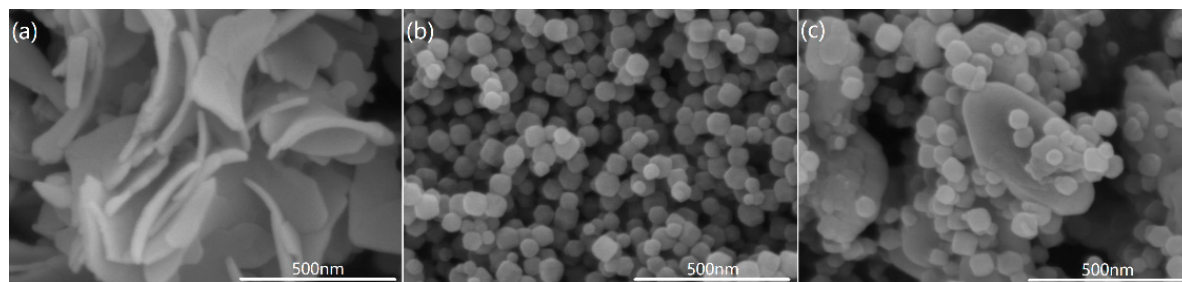


Figure 2. SEM images of (a) BVO, (b) ZIF-8, and (c) ZIF-8@BVO.

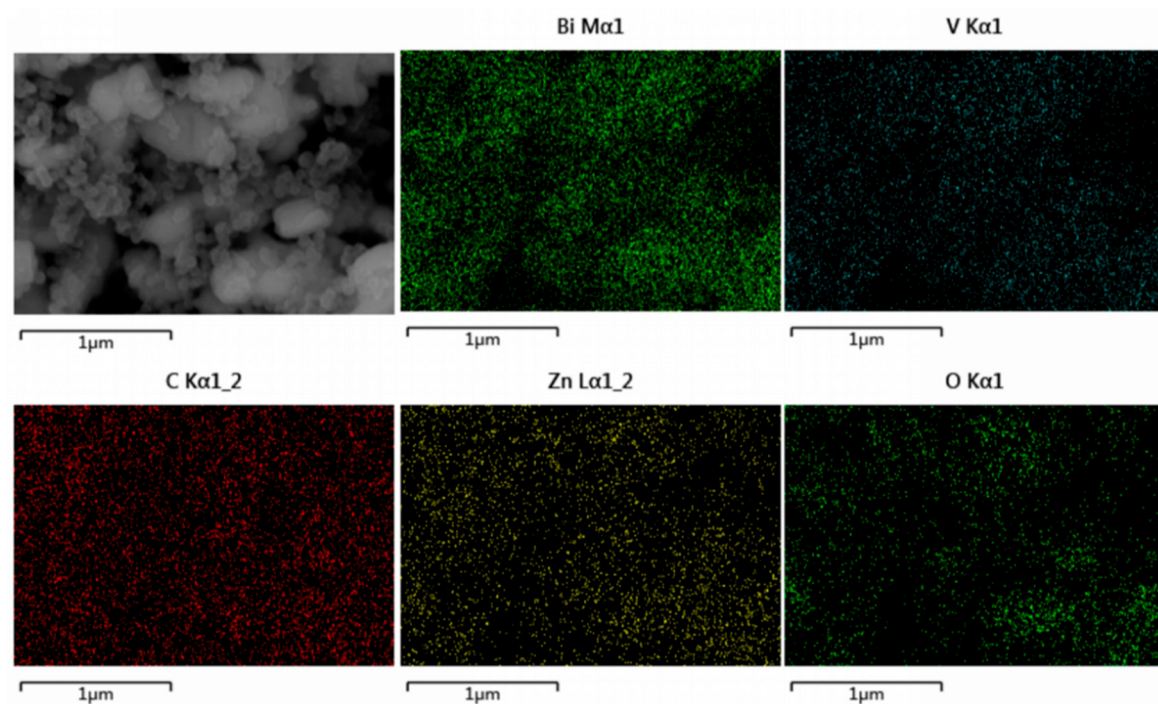


Figure 3. Energy dispersive spectroscopy (EDS) element mapping of ZIF-8@BVO composite.

3.2. Analysis of $\cdot\text{OH}$ Radical

Figure 4 shows the PL spectrum of the TA solution after 100 min under visible light irradiation. In the blank control group, no PL signal was detected because no photocatalyst was added. After adding BVO photocatalyst, an obvious peak was detected at 425 nm, which proved the formation of hydroxyl radical [29]. The PL intensity at 425 nm increased significantly with the addition of the same mass of the composite catalyst, indicating that more hydroxyl radicals were produced compared with BVO. More hydroxyl radicals with strong oxidation can effectively promote the photocatalytic degradation of organic pollutants.

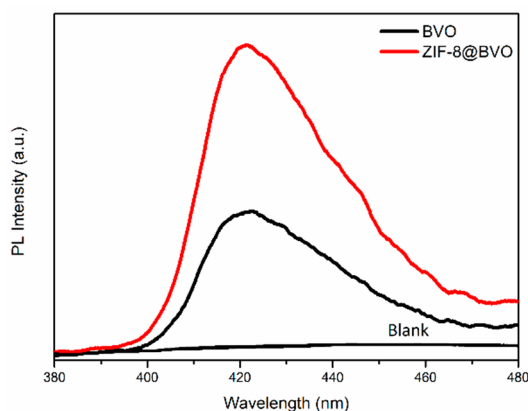


Figure 4. Photoluminescence spectra of the terephthalic acid (TA) solution after irradiating for 100 min.

3.3. Photocatalytic Performance

The photocatalytic performance of pure BVO and ZIF-8@BVO composite were evaluated by the photodegradation of MB aqueous solution under visible light irradiation, and the degradation curves and efficiencies are shown in Figure 5a–b. As seen in Figure 5b, it is obvious that the photocatalytic activity of ZIF-8@BVO composite was enhanced compared with that of the mixture of BVO and ZIF-8. The photodegradation efficiency of MB reached 80% within 130 min. For comparative analysis, a blank

test was carried out without any photocatalyst, which showed that only 1.5% of MB was photolyzed. In order to accurately determine the adsorption properties of ZIF-8@BVO composite for MB under darkness, we took samples every 5 min for measurement within the initial 30 min. The results in Figure 5c show that the adsorption of MB reached equilibrium after 25 min in a dark environment, and no more MB was adsorbed in the subsequent process. The superior photocatalytic activity of ZIF-8@BVO composite should be ascribed to the enhanced absorption ability of MB molecules as well as improved migration and separation efficiency of photogenerated carriers resulting from the synergistic effect between ZIF-8 and BVO. BVO-loaded ZIF-8 can not only improve the adsorption capacity of pollutants, but can also effectively enhance the separation of photogenerated electron-hole pairs. Due to the difference in energy band positions, ZIF-8 and BVO form a heterojunction at the contact interface, which can promote the transformation of photogenerated charges under the effect of the built-in electric field. The photogenerated holes in the valence band (+2.4 V vs. NHE) of BVO [30] migrate to the conduction band of ZIF-8 (+1.9 V vs. NHE) [31], thus effectively inhibiting the recombination of photogenerated electrons and holes. Furthermore, the stability of photocatalyst is very important for practical application. Figure 5d shows the photocatalytic degradation efficiencies of the reused composite and the mixture. The reaction activities of ZIF-8@BVO composite and the mixture decreased by about 3% and 4% respectively after three recycling tests, which proved that the composite photocatalyst had good stability during the photocatalytic process. In addition, the XRD patterns of ZIF-8@BVO composite before and after three cycles are shown in Figure 6. There was no obvious change in the diffraction peaks, suggesting that the synthesized composite possessed a highly stable structure.

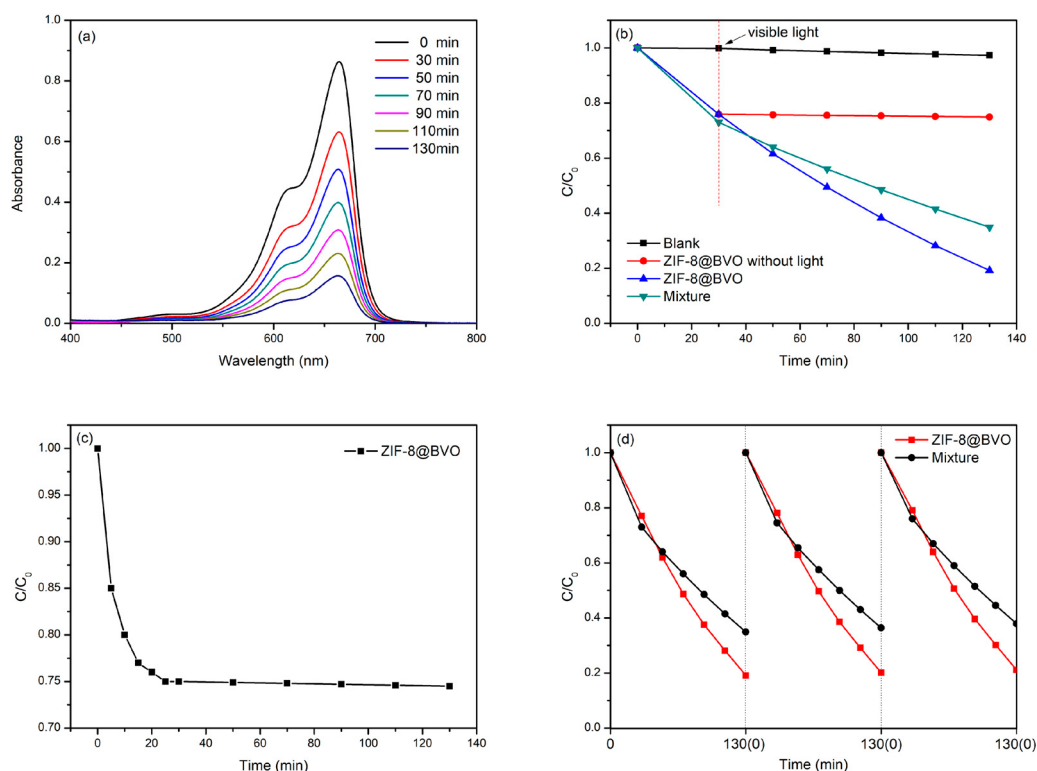


Figure 5. (a) Time-dependent UV-Vis spectrum of methylene blue (MB) solution photodegraded by ZIF-8@BVO composite; (b) photocatalytic degradation efficiencies of MB; (c) adsorption efficiency of ZIF-8@BVO composite under darkness; (d) photocatalytic recyclability efficiencies of ZIF-8@BVO composite and the mixture.

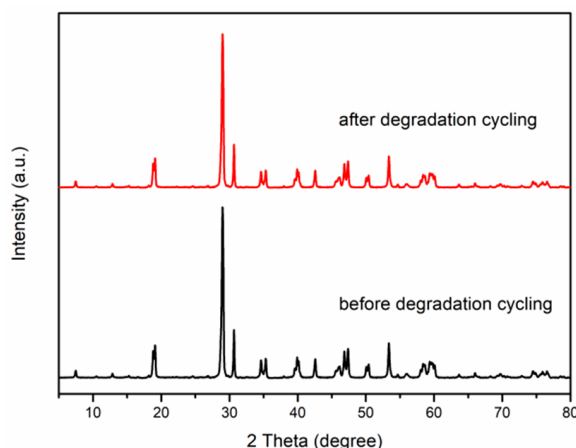


Figure 6. XRD patterns of ZIF-8@BVO composite before and after three cycles.

3.4. Proposed Mechanism for the Enhanced Photocatalytic Performance

In general, photogenerated electron–hole pairs are produced when the energy of incident photons is greater than the band-gap energy of photocatalysts. The electrons in the valence band will transfer to the conduction band and become conduction electrons (e^-), leaving a hole (h^+) at the valence band [32]. Photogenerated electrons have strong reducibility, and holes are highly oxidizing, which can react with substances adsorbed on the surface of photocatalysts. In the photocatalytic process, most of the photogenerated electrons and holes will recombine inside the catalyst, and partial holes migrated to the surface of the catalyst will directly decompose MB, or react with the adsorbed H_2O to generate hydroxyl radicals to participate in MB degradation. Meanwhile, the remaining electrons will react with O_2 to form O_2^- and then react with protons to form HOO. Further reaction will produce *OH , and participate in the degradation of MB [33]. As photocatalysis occurs on the surface of the photocatalyst, the enhanced adsorption capacity of dye molecules is conducive to the rapid progress of the photocatalytic reaction. According to BET method, the specific surface areas of BVO, ZIF-8, and ZIF-8@BVO were calculated to be 2.3, 1179.6, and 249.1 m^2/g , respectively. Compared with pure BVO, the specific surface area of ZIF-8@BVO composite photocatalyst to MB molecules improved significantly due to the unique pore structure and large specific surface area of ZIF-8, which will be beneficial to the photocatalytic process. On the other hand, the separation and migration efficiency of photogenerated electrons and holes are promoted by the synergistic effect of BVO and ZIF-8, which reduces the recombination of photogenerated electrons and holes, and more active species participate in the photocatalytic process.

4. Conclusions

In summary, a novel ZIF-8@BiVO₄ composite photocatalyst was successfully synthesized by a facile in-situ growth method. Compared with the mixture of BVO and ZIF-8, the composite photocatalyst showed superior photocatalytic performance for the degradation of MB under visible light irradiation. Experiment results proved that the enhanced photocatalytic performance could be ascribed to the decreased recombination of photogenerated electrons and holes owing to the synergistic effect between BVO and ZIF-8. Moreover, the recycling tests showed that the composite photocatalyst possessed good photostability. This study could provide a new strategy for the development of highly efficient photocatalysts for wastewater treatment.

Author Contributions: Y.-y.L. conceived and designed the experiments; Y.-h.S. performed the experiments and wrote the manuscript; Y.X., S.-k.S., X.-b.X., X.-r.Z. and J.Z. contributed reagents/materials/analysis tools.

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References

- Hoffmann, M.R.; Martin, S.T.; Choi, E.; Bahnemann, D.W. Environmental applications of semiconductor photocatalysis. *Chem. Rev.* **1995**, *95*, 69–96. [[CrossRef](#)]
- Bai, X.; Wang, L.; Zong, R.; Zhu, Y. Photocatalytic activity enhanced via g-C₃N₄ nanoplates to nanorods. *J. Phys. Chem. C* **2013**, *117*, 9952–9961. [[CrossRef](#)]
- Choi, J.; Park, H.; Hoffmann, M. Effects of single metal-ion doping on the visible-light photoreactivity of TiO₂. *J. Phys. Chem. C* **2010**, *114*, 783–792. [[CrossRef](#)]
- Si, Y.H.; Xia, Y.; Shang, S.K.; Xiong, X.B.; Zeng, X.R.; Zhou, J.; Li, Y.Y. Enhanced visible light driven photocatalytic behavior of BiFeO₃/reduced graphene oxide composites. *Nanomaterials* **2018**, *8*, 526. [[CrossRef](#)] [[PubMed](#)]
- Si, Y.H.; Xia, Y.; Li, Y.Y.; Shang, S.K.; Xiong, X.B.; Zeng, X.R.; Zhou, J. Enhanced visible-active photocatalytic behaviours observed in Mn-doped BiFeO₃. *Mod. Phys. Lett. B* **2018**, *32*, 1850185. [[CrossRef](#)]
- Jia, T.K.; Li, J.L.; Long, F.; Zhao, J.W.; Deng, Z.; Wang, X.H.; Zhang, Y. Ultrathin g-C₃N₄ nanosheet-modified BiOCl hierarchical flower-like plate heterostructure with enhanced photostability and photocatalytic performance. *Crystals* **2017**, *7*, 266. [[CrossRef](#)]
- Guo, M.N.; He, Q.L.; Wang, A.Y.; Wang, W.M.; Fu, Z.Y. A novel, simple and green way to fabricate BiVO₄ with excellent photocatalytic activity and its methylene blue decomposition mechanism. *Crystals* **2016**, *6*, 81. [[CrossRef](#)]
- Yu, J.Q.; Kudo, A. Effects of structural variation on the photocatalytic performance of hydrothermally synthesized BiVO₄. *Adv. Funct. Mater.* **2010**, *16*, 2163–2169. [[CrossRef](#)]
- Dong, S.Y.; Feng, J.L.; Li, Y.K.; Hu, L.M.; Liu, M.L.; Wang, Y.F.; Pi, Y.Q.; Sun, J.Y.; Sun, J.H. Shape-controlled synthesis of BiVO₄ hierarchical structures with unique natural-sunlight-driven photocatalytic activity. *Appl. Catal. B Environ.* **2014**, *152–153*, 413–424. [[CrossRef](#)]
- Ho-Kimura, S.; Moniz, S.J.A.; Handoko, A.D.; Tang, J.W. Enhanced photoelectrochemical water splitting by nanostructured BiVO₄-TiO₂ composite electrodes. *J. Mater. Chem. A* **2014**, *2*, 3948–3953. [[CrossRef](#)]
- Jo, W.J.; Jang, J.W.; Kong, K.; Kang, H.J.; Kim, J.Y.; Jun, H.; Parmar, K.P.S.; Lee, J.S. Phosphate doping into monoclinic BiVO₄ for enhanced photoelectrochemical water oxidation activity. *Angew. Chem. Int. Ed.* **2012**, *51*, 3147–3151. [[CrossRef](#)] [[PubMed](#)]
- Regmi, C.; Dhakal, D.; Lee, S.W. Visible-light-induced Ag/BiVO₄ semiconductor with enhanced photocatalytic and antibacterial performance. *Nanotechnology* **2017**, *29*, 1416–1426. [[CrossRef](#)] [[PubMed](#)]
- Appavu, B.; Thiripuranthagan, S.; Ranganathan, S.; Erusappan, E.; Kannal, K. BiVO₄/N-rGO nano composites as highly efficient visible active photocatalyst for the degradation of dyes and antibiotics in eco system. *Ecotoxicol. Environ. Saf.* **2018**, *151*, 118–126. [[CrossRef](#)] [[PubMed](#)]
- Xuan, W.; Zhu, C.; Liu, Y.; Cui, Y. Mesoporous metal-organic framework materials. *Chem. Soc. Rev.* **2012**, *41*, 1677–1695. [[CrossRef](#)] [[PubMed](#)]
- Furukawa, H.; Ko, N.; Go, Y.B.; Aratani, N.; Choi, S.B.; Choi, E.; Yazaydin, A.O.; Snurr, R.Q.; O’Keeffe, M.; Kim, J.; et al. Ultrahigh porosity in metal-organic frameworks. *Science* **2010**, *329*, 424–428. [[CrossRef](#)] [[PubMed](#)]
- Wang, C.; Xie, Z.G.; deKrafft, K.E.; Lin, W.L. Doping metal-organic frameworks for water oxidation, carbon dioxide reduction, and organic photocatalysis. *J. Am. Chem. Soc.* **2011**, *133*, 13445–13454. [[CrossRef](#)] [[PubMed](#)]
- Wang, J.L.; Wang, C.; Lin, W.B. Metal-organic frameworks for light harvesting and photocatalysis. *ACS Catal.* **2012**, *2*, 2630–2640. [[CrossRef](#)]

18. Li, B.; Wen, H.M.; Cui, Y.J.; Zhou, W.; Qian, G.D.; Chen, B.L. Emerging multifunctional metal-organic framework materials. *Adv. Mater.* **2016**, *28*, 8819–8860. [[CrossRef](#)] [[PubMed](#)]
19. Du, X.D.; Yi, X.H.; Wang, P.; Zheng, W.W.; Deng, J.G.; Wang, C.C. Robust photocatalytic reduction of Cr(VI) on UiO-66-NH₂(Zr/Hf) metal-organic framework membrane under sunlight irradiation. *Chem. Eng. J.* **2019**, *356*, 393–399. [[CrossRef](#)]
20. Samuel, M.S.; Bhattacharya, J.; Parthiban, C.; Viswanathan, G.; Singh, N.D.P. Ultrasound-assisted synthesis of metal organic framework for the photocatalytic reduction of 4-nitrophenol under direct sunlight. *Ultrason. Sonochem.* **2018**, *49*, 215–221. [[CrossRef](#)] [[PubMed](#)]
21. Lee, Y.; Kim, J.; Ahn, W. Synthesis of metal-organic frameworks: A mini review. *Korean J. Chem. Eng.* **2013**, *30*, 1667–1680. [[CrossRef](#)]
22. Nguyen, L.T.L.; Le, K.K.A.; Phan, N.T.S. A zeolite imidazolate framework ZIF-8 catalyst for friedel-crafts acylation. *Chin. J. Catal.* **2012**, *33*, 688–696. [[CrossRef](#)]
23. Lu, G.; Hupp, J.T. Metal-organic frameworks as sensors: A ZIF-8 based Fabry-Pérot device as a selective sensor for chemical vapors and gases. *J. Am. Chem. Soc.* **2010**, *132*, 7832. [[CrossRef](#)] [[PubMed](#)]
24. Huang, H.L.; Zhang, W.J.; Liu, D.H.; Liu, B.; Chen, G.J.; Zhong, C.L. Effect of temperature on gas adsorption and separation in ZIF-8: A combined experimental and molecular simulation study. *Chem. Eng. Sci.* **2011**, *66*, 6297–6305. [[CrossRef](#)]
25. Park, K.S.; Ni, Z.N.; Cote, A.P.; Choi, J.Y.; Huang, R.; Uribe-Romo, F.J. Exceptional chemical and thermal stability of zeolitic imidazolate frameworks. *Proc. Natl. Acad. Sci. USA* **2006**, *103*, 10186–10191. [[CrossRef](#)] [[PubMed](#)]
26. Zhang, L.; Chen, D.R.; Jiao, X.L. Monoclinic structured BiVO₄ nanosheets: Hydrothermal preparation, formation mechanism, and coloristic and photocatalytic properties. *J. Phys. Chem. B* **2006**, *110*, 2668–2673. [[CrossRef](#)] [[PubMed](#)]
27. Sanchez-Lainez, J.; Zornoza, B.; Friebe, S.; Caro, J.; Cao, S.; Sabetghadam, A.; Seoane, B.; Gascon, J.; Kapteijn, F.; Le Guillouzer, C.; et al. Influence of ZIF-8 particle size in the performance of polybenzimidazole mixed matrix membranes for pre-combustion CO₂ capture and its validation through interlaboratory test. *J. Membr. Sci.* **2016**, *515*, 45–53. [[CrossRef](#)]
28. Zhang, L.J.; Li, S.; Liu, B.K.; Wang, D.J.; Xie, T.F. Highly Efficient CdS/WO₃ photocatalysts: Z-scheme photocatalytic mechanism for their enhanced photocatalytic H₂ evolution under visible light. *ACS Catal.* **2014**, *4*, 3724–3729. [[CrossRef](#)]
29. Ma, D.D.; Shi, J.W.; Zou, Y.J.; Fan, Z.Y.; J, X.; Niu, C.M. Highly efficient photocatalyst based on a CdS quantum dots/ZnO nanosheets 0D/2D heterojunction for hydrogen evolution from water splitting. *ACS Appl. Mater. Interfaces* **2017**, *9*, 25377–25386. [[CrossRef](#)] [[PubMed](#)]
30. Li, J.H.; Bai, J.; Niu, X.H.; Li, X.Y.; Chen, S.; Wang, J.C.; Zhou, B.X. Dramatic enhancement of photocurrent for BiVO₄/TiO₂ heterojunction photoanode with suitable band-match via in-situ band regulation using Ta. *Int. J. Hydrogen Energy* **2018**, *43*, 18202–18210. [[CrossRef](#)]
31. Chin, M.; Cisneros, C.; Araiza, S.M.; Vargas, K.M.; Ishihara, K.M.; Tian, F.Y. Rhodamine B degradation by nanosized zeolitic imidazolate framework-8 (ZIF-8). *RSC Adv.* **2018**, *8*, 26987–26997. [[CrossRef](#)] [[PubMed](#)]
32. Zhou, P.; Yu, J.G.; Jaroniec, M. All-solid-state Z-scheme photocatalytic systems. *Adv. Mater.* **2014**, *26*, 4920–4935. [[CrossRef](#)] [[PubMed](#)]
33. Wu, T.X.; Liu, G.M.; Zhao, J.C.; Hidaka, H.; Serpone, N. Photoassisted degradation of dye pollutants. V. self-photosensitized oxidative transformation of rhodamine B under visible light irradiation in aqueous TiO₂ dispersions. *J. Phys. Chem. B* **1998**, *102*, 5845–5851. [[CrossRef](#)]

