

Article

Synergistic Effect of Fe Doping and Oxygen Vacancies on the Optical Properties and CO₂ Reduction Mechanism of Bi₄O₅Br₂

Gaihui Liu ¹, Xie Huang ¹, Shuaishuai Liu ², Xiangzhou Yan ³, Nan Dong ⁴, Huihui Shi ⁴, Fuchun Zhang ^{4,*} and Suqin Xue ^{1,*}

¹ Network Information Center, Yan'an University, Yan'an 716000, China; liugaihui@yau.edu.cn (G.L.); hx@yau.edu.cn (X.H.)

² School of Petroleum Engineering and Environmental Engineering, Yan'an University, Yan'an 716000, China; i15829419647@163.com

³ New Energy Department of CNOOC (China), Beijing 100010, China; yanxzh2@cnooc.com.cn

⁴ School of Physics and Electronic Information, Yan'an University, Yan'an 716000, China; dongnan@yau.edu.cn (N.D.); shihui@yau.edu.cn (H.S.)

* Correspondence: yadxzfc@yau.edu.cn (F.Z.); ydxsq@yau.edu.cn (S.X.)

Abstract

In this study, the synergistic effects of Fe doping and oxygen vacancies on the structural, electronic, and optical properties of Bi₄O₅Br₂, as well as their influence on the photocatalytic CO₂ reduction mechanism, were systematically explored through first-principles calculations. The results reveal that Fe-doped, oxygen-defective, and Fe–Vo co-modified Bi₄O₅Br₂ systems exhibit excellent thermodynamic and dynamic stability. Oxygen vacancies introduce defect states near the Fermi level, narrowing the band gap and enhancing charge localization and CO₂ adsorption, while Fe doping induces strong spin polarization and introduces Fe 3*d* impurity levels that effectively couple with O 2*p* orbitals, promoting charge transfer and visible-light absorption. The coexistence of Fe dopants and oxygen vacancies produces a significant synergistic effect, forming a continuous energy-level bridge that enhances charge separation and broadens the light absorption range. Gibbs free energy analyses further demonstrate that the Fe–Vo–BOB system exhibits the lowest energy barriers and the most favorable thermodynamics for CO₂-to-CO conversion. This study provides deep insight into the defect–dopant synergy in Bi₄O₅Br₂ and offers valuable theoretical guidance for engineering highly efficient visible-light-driven photocatalysts in solar energy conversion and environmental remediation.

Keywords: Bi₄O₅Br₂; DFT calculations; Fe doping; oxygen vacancies; synergistic effect

Academic Editor: Subhash Sharma

Received: 29 November 2025

Revised: 30 January 2026

Accepted: 9 February 2026

Published: 11 February 2026

Copyright: © 2026 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the [Creative Commons Attribution \(CC BY\)](https://creativecommons.org/licenses/by/4.0/) license.

1. Introduction

Recently, the global energy threat and environmental challenges have grown increasingly severe. In particular, the large-scale combustion of fossil fuels has led to excessive CO₂ emissions, which are widely recognized as one of the primary drivers of global warming and ecological imbalance [1,2]. Efficient capture and utilization of CO₂ are therefore of great significance, not only for mitigating the greenhouse effect but also for achieving carbon neutrality and sustainable development. Photocatalytic CO₂ reduction is regarded as one of the most promising green energy technologies among numerous CO₂ conversion and utilization techniques [3–5]. This is due to its ability to

directly harness solar energy to convert CO₂ into high-value-added carbon-based fuels such as CO, CH₄, and CH₃OH. However, current photocatalytic CO₂ reduction still suffers from several intrinsic limitations, including insufficient light absorption, severe charge carrier recombination, and high reaction energy barriers. Hence, the exploitation of novel and highly efficient photocatalysts has emerged as a central focus in this research field [6,7].

Bismuth-based oxyhalides (BiOX, X = Cl, Br, I) have attracted increasing attention as promising photocatalysts due to their unique layered architectures and outstanding electronic characteristics [8,9]. Nevertheless, their practical applications remain constrained by the mismatch between the conduction band position and redox potentials as well as by the low efficiency of charge carrier separation. From the viewpoint of electronic band structure, the valence band of BiOX predominantly consists of hybridized O 2*p* and X *np* orbitals, whereas the conduction band is mainly contributed by Bi 6*p* orbitals [10,11]. Modulating the Bi/O/X ratio (Bi_{1-x}O_yX_z) tunes the band structure (gap and band edges), thereby improving reduction capability and overall photocatalytic performance. Within the BiOX family, Bi₄O₅Br₂ possesses a layered architecture consisting of alternating [Bi₂O₂]²⁺ slabs and Br₂²⁻ layers, which imparts excellent visible-light absorption and a pronounced internal electric field [12,13]. Compared with BiOBr and BiOCl, Bi₄O₅Br₂ exhibits a lower carrier recombination rate and superior photochemical stability, demonstrating outstanding performance in pollutant degradation, hydrogen evolution, and CO₂ reduction reactions [14–16]. However, its photocatalytic efficiency remains restricted by insufficient visible-light utilization arising from its intrinsic band-gap characteristics. Moreover, excessive band narrowing tends to exacerbate carrier recombination, while the insufficient CO₂ adsorption and activation ability leads to high reaction energy barriers [17]. Consequently, improving the electronic structure and surface chemical properties through appropriate modification strategies has become essential for boosting its photocatalytic performance.

Defect engineering has proven to be an effective strategy for improving photocatalytic performance. For Bi-based oxyhalides (BiOBr_{1-x}I_x), the introduction of oxygen vacancies (V_o) not only generates defect states within the band gap to extend light absorption into the visible region, but also serves as electron-trapping centers, which effectively suppress electron-hole recombination and prolong carrier lifetimes, improving charge separation efficiency [18]. In addition, the presence of oxygen vacancies can significantly enhance the adsorption and activation of CO₂, lower the reaction energy barriers, and accelerate surface reaction kinetics [19,20]. Oxygen vacancies in oxides can exist in multiple charge states. Depending on the Fermi level and local compensation, an oxygen vacancy may appear as an empty doubly charged vacancy (V_o²⁺), a singly occupied vacancy (V_o[•]), often referred to as an F[•] center), or a doubly occupied neutral vacancy (V_o⁰, an F center). These charge states exhibit distinct optical signatures, paramagnetic (notably for F[•]), and different diffusion/thermal-stability behaviors, which should be distinguished when interpreting defect-induced electronic/optical responses [21,22]. Furthermore, transition metal doping represents another promising strategy to optimize the performance of Bi₄O₅Br₂. Introducing transition metals (e.g., Fe, Mn, Co, and Ni) can adjust the local electronic structure, improve carrier mobility, and fine-tune the band-edge positions to optimize the reduction reaction energetics [23]. In particular, Fe [24,25], Mn [26,27], and Ni [28,29] doping has been demonstrated to narrow the band gap and induce a significant red-shift in the absorption edge, thereby improving visible-light harvesting of Bi₄O₅Br₂. Meanwhile, the introduction of metal 3*d* impurity levels facilitate charge carrier separation and migration, suppressing electron-hole recombination and generating additional surface-active sites. Therefore, Bi₄O₅Br₂ modified with transition-metal dopants displays significantly enhanced photocatalytic efficiency in both CO₂ reduction and pollutant degradation. Similar dopant–vacancy coupling effects have been reported in Fe-

doped BiOCl nanosheets with oxygen vacancies and Fe-BiOBr composites enriched with surface oxygen vacancies, highlighting the general importance of Fe–Vo regulation in Bi-based oxyhalides [30].

Building on the above analysis, this study employs first-principles calculations to comprehensively explore the electronic structure, optical properties, and CO₂ reduction mechanism of Bi₄O₅Br₂ under defect and doping regulation. First, the intrinsic Bi₄O₅Br₂ was analyzed in terms of its lattice parameters, band structure, density of states, optical absorption spectrum, and dielectric function to clarify its fundamental physical characteristics. Then, a single oxygen vacancy was introduced to explore its effects on band structure tuning, electronic state redistribution, and optical properties, as well as to elucidate the role of defect levels in promoting charge-carrier separation. On this basis, the influence of Fe doping was further examined, elucidating its advantages in band gap modulation and enhancement of visible-light absorption. And finally, the combined influence of oxygen vacancies and Fe doping was thoroughly examined. By comparing the CO₂ reduction energy barriers under different modification strategies, the kinetic advantages of the synergistic regulation were revealed, offering insights into the photocatalytic CO₂ reduction mechanism of defect-engineered and doped Bi₄O₅Br₂. Motivated by the above gap, previous transition-metal-doped Bi₄O₅Br₂ studies (e.g., Ni/Mn/Co or Fe doping) mainly discussed the role of single dopants, while the coupled dopant–defect (Fe–Vo) synergy and its mechanistic impact on both optical response and CO₂ reduction energetics remain insufficiently clarified. In this work, we go beyond single-dopant descriptions by constructing a consistent set of models (pristine, Fe-doped, Vo-containing, and Fe–Vo coupled Bi₄O₅Br₂) and comparing them under the same computational framework. This enables us to explicitly reveal how the Fe–Vo coupled defect modulates the electronic structure/optical absorption and facilitates the CO₂ → CO pathway, thereby providing a clear mechanistic basis for defect–dopant co-engineering in Bi-based oxyhalides [31].

2. Computational Details

All calculations in this work were carried out within the framework of density functional theory (DFT) using the Device Studio integrated Projector Augmented-Wave (DS-PAW) method package [32]. The electronic wave functions were represented by a plane-wave basis set with a cutoff energy of 450 eV. The convergence thresholds for total energy and atomic forces were set to 1×10^{-5} eV and 0.05 eV/Å, respectively. A $4 \times 7 \times 4$ Monkhorst-Pack k-point mesh was employed to sample the Brillouin zone. Exchange-correlation effects were described using the Perdew–Burke–Ernzerhof (PBE) functional under the generalized gradient approximation (GGA) [33,34], and the calculation precision was set to ‘Accurate’. Unless otherwise stated, oxygen vacancies were modeled in a charge-neutral supercell ($q = 0$). Surface slab model for CO₂ adsorption and CO₂RR. CO₂ adsorption and reaction calculations were performed on the Bi₄O₅Br₂ (020) surface. The slab was generated by cleaving the bulk along (020) with the top position set to fractional 2.964 and a slab thickness of 4.0 Å (corresponding to ‘Thickness = 21.82 Å’ in the Angstrom scale), without bond capping. A vacuum spacing of ~21.82 Å was added along the surface normal to avoid spurious interactions between periodic images.

To accurately capture the electronic correlations of the Fe 3*d* states, the DFT+U method was applied to the Fe-doped systems. The U value for Fe 3*d* orbitals was set to 3.3 eV [35], based on previous studies and to better describe the localized nature of the Fe 3*d* states. This correction helps address the self-interaction errors typically associated with DFT for transition metal systems, and improves the accuracy of the electronic structure, especially in terms of magnetic properties, charge transfer, and optical properties.

For CO₂ adsorption, only one adsorption configuration was considered (no multi-site screening). To enable a consistent energetic comparison among BOB, Vo–BOB, Fe–BOB,

and Fe–Vo–BOB, the slab orientation/termination, thickness, vacuum size, and the bottom-fixed constraint scheme were kept identical. During geometry optimizations, atoms in a bottom slab region (with a prescribed thickness along the surface normal) were fixed to mimic the bulk, while all remaining atoms and adsorbates were fully relaxed.

Dipole correction. Dipole corrections were not applied in our slab calculations (LDIPOL was not enabled) because the constructed (020) slab adopts effectively symmetric termination along the surface normal; thus, no significant net dipole is expected in the vacuum direction.

Ab initio molecular dynamics (AIMD). AIMD simulations were performed at 300 K with a constant target temperature (TEBEG = TEEND = 300 K). The time step was 1.0 fs (POTIM = 1.0), and each trajectory was propagated for 6000 steps (NSW = 6000), corresponding to a total simulation time of ~6 ps. The simulations were carried out using IBRION = 0 (Born–Oppenheimer AIMD) in the NVT ensemble controlled by a Nosé-type thermostat (SMASS = 0.02), with a fixed simulation cell (constant volume). An initial equilibration stage was observed at the beginning of the trajectory; after equilibration, the temperature fluctuates around the target value (e.g., an average of ~300 K over the last ~5 ps), and the equilibrated part of the trajectory was used for stability assessment.

In the model construction, all calculations were performed based on the intrinsic $\text{Bi}_4\text{O}_5\text{Br}_2$ supercell (Figure 1a), containing 16 Bi, 20 O, and 8 Br atoms. On this basis, Fe-doped and defect-engineered models were constructed. For Fe doping, Fe was introduced substitutionally at Bi sites, and four symmetry-inequivalent Fe configurations (Fe–BOB-1 to Fe–BOB-4; Figure 1b–e) were considered to evaluate the effects of dopant position and local coordination environment. Specifically, these configurations cover two Fe substitutions on the same side/plane versus opposite sides/planes, and within each category, adjacent (sharing/neighbor O coordination) versus separated placements, including symmetric and asymmetric substitution positions. The most stable configuration (Fe–BOB-1) was selected for subsequent property calculations. In addition, an oxygen-vacancy model was built by removing one O atom from $\text{Bi}_4\text{O}_5\text{Br}_2$ (Figure 1f). For the coupled Fe–Vo system, the oxygen vacancy was created in Fe–BOB-1 by removing an O atom directly coordinated to the two Fe dopants, to probe the nearest-neighbor Fe–Vo interaction (Figure 1g) and systematically evaluate the synergistic effect of simultaneous doping and defect engineering on the electronic structure and physicochemical properties of $\text{Bi}_4\text{O}_5\text{Br}_2$. This Fe-adjacent vacancy model is physically motivated, since Fe-oxygen-vacancy coupling in Bi-based oxyhalides has been reported to strongly modulate charge separation and surface reactivity (e.g., Fe-doped BiOCl with oxygen vacancies) [30,36].

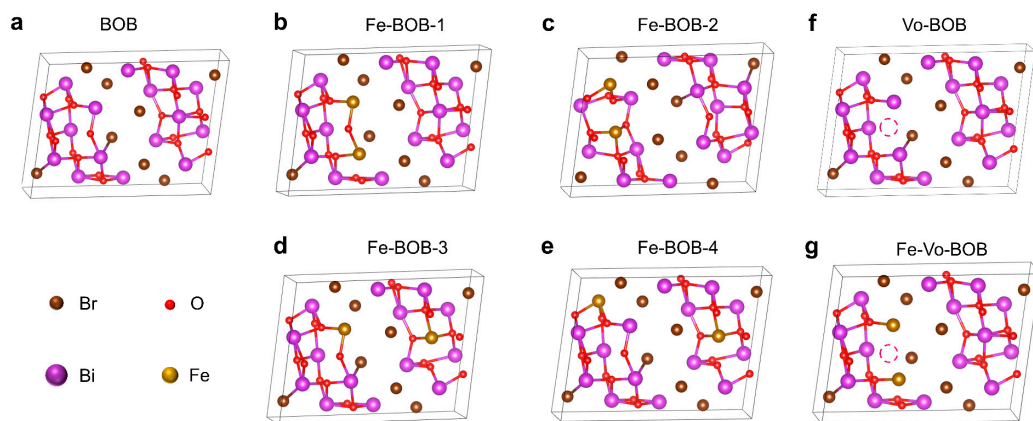


Figure 1. The models of (a) pure $\text{Bi}_4\text{O}_5\text{Br}_2$, (b–e) Fe-doped $\text{Bi}_4\text{O}_5\text{Br}_2$, (f) $\text{Bi}_4\text{O}_5\text{Br}_2$ with oxygen vacancies, and (g) Fe-doped $\text{Bi}_4\text{O}_5\text{Br}_2$ with oxygen vacancies.

3. Results and Discussion

3.1. Formation Energy

Based on the optimized structures, the formation energies (ΔE_{Fe}) of four distinct Fe-doped $\text{Bi}_4\text{O}_5\text{Br}_2$ models were calculated using the equation below [37,38]:

$$\Delta E_{\text{Fe}} = E_{\text{X-BOB}} - E_{\text{BOB}} + 2E_{\text{Bi}} - 2E_{\text{Fe}} \quad (1)$$

where $E_{\text{X-BOB}}$ is the total energy (eV) of Fe-doped $\text{Bi}_4\text{O}_5\text{Br}_2$, E_{BOB} refers to the total energy (eV) of pristine $\text{Bi}_4\text{O}_5\text{Br}_2$, while E_{Fe} and E_{Bi} correspond to the energies (eV) of a single Fe atom and a Bi ion, respectively. As summarized in Table 1, the Fe-BOB-1 model exhibited the lowest formation energy of 0.685 eV, indicating its superior thermodynamic stability. Therefore, the Fe-BOB-1 configuration was selected as the representative structure for subsequent calculations and property analyses in this study.

Table 1. Formation energy of different Fe-doped $\text{Bi}_4\text{O}_5\text{Br}_2$ configurations.

Configuration	Fe-BOB-1	Fe-BOB-2	Fe-BOB-3	Fe-BOB-4
Fe- $\text{Bi}_4\text{O}_5\text{Br}_2$	−40,451.727733	−40,451.623687	−40,451.492143	−40,451.26327
$\text{Bi}_4\text{O}_5\text{Br}_2$	−43,175.60554	−43,175.60554	−43,175.60554	−43,175.60554
Fe	−601.825309	−601.825309	−601.825309	−601.825309
Bi	−1963.421754	−1963.421754	−1963.421754	−1963.421754
Energy (eV)	0.6849205	0.7889665	0.9205105	1.1493855

Structural stability under thermal perturbations was assessed for the Vo-BOB, Fe-BOB, and Fe-Vo-BOB models by ab initio molecular dynamics (AIMD) at 300 K. As shown in Figure 2, all structures remain intact over the simulation without signs of structural collapse. Quantitatively, the equilibrated trajectories exhibit bounded RMSD values (Table S2): 0.397 ± 0.070 Å (max 0.514 Å) for Vo-BOB, 0.476 ± 0.085 Å (max 0.663 Å) for Fe-BOB, and 0.875 ± 0.418 Å (max 1.464 Å) for Fe-Vo-BOB, indicating only thermal vibrations around the equilibrated configurations. Meanwhile, the temperature fluctuates around the target value (300 K), and the total energy E_{tot} (electron + ion + thermostat) fluctuates around a stable mean with no pronounced drift over the production segment (Table S2). These results support the thermodynamic/dynamic stability of the defect/doped $\text{Bi}_4\text{O}_5\text{Br}_2$ models under thermal perturbation [39].

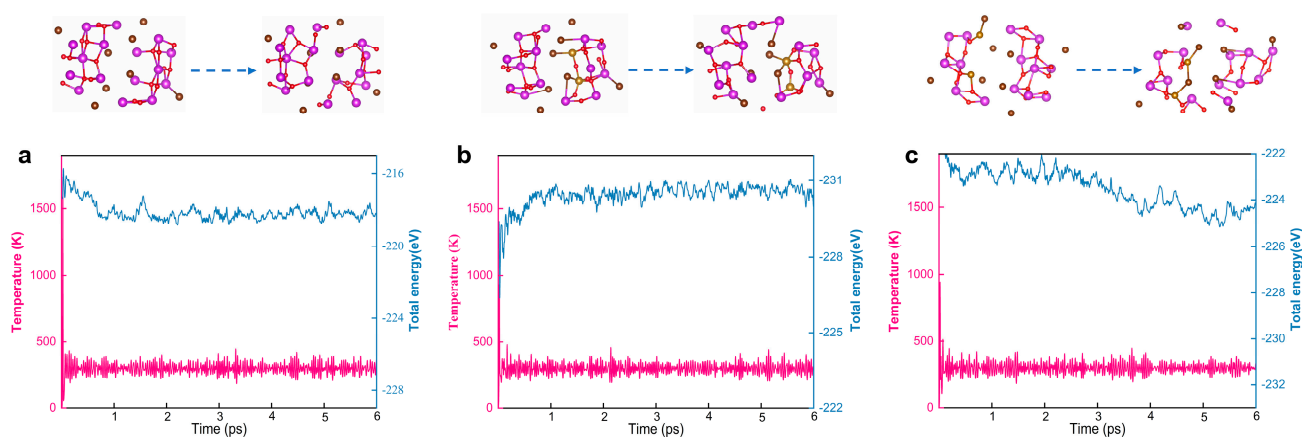


Figure 2. AIMD simulation results of (a) Vo-BOB, (b) Fe-BOB, and (c) Fe-Vo-BOB models.

3.2. Electron Localization Function

The electron localization function (ELF) quantifies the likelihood of finding two electrons with the same spin in close proximity and is thus widely used to evaluate electron localization and to elucidate the nature of chemical bonding in materials [40,41]. As demonstrated in Figure 3a, the ELF distributions revealed that in pristine $\text{Bi}_4\text{O}_5\text{Br}_2$, electrons were primarily localized around O atoms, exhibiting a pronounced O-Bi covalent bonding feature. Conversely, the electron density within the Br layer exhibited a more delocalized character. This indicated that the interlayer interactions were mainly governed by ionic bonding and van der Waals forces, endowing the overall structure with high stability. Upon introducing an oxygen vacancy (Figure 3b), electron localization near the defect region was enhanced, with partial electron redistribution toward adjacent Bi atoms, resulting in an asymmetric local charge density and the formation of potential reactive sites. In the Fe-doped system (Figure 3c), a significant increase in electron density was observed around the Fe atoms, and the Fe-O bond region exhibited strong electronic localization, collectively confirming the effective Fe $3d$ and O $2p$ orbital hybridization. This hybridization enhanced $\text{Bi}_4\text{O}_5\text{Br}_2$ charge polarization and carrier transport properties [28,42]. When Fe doping coexisted with oxygen vacancies (Figure 3d), electrons underwent synergistic redistribution among Fe, Bi, and defect regions, forming new localized charge-rich zones with stronger electronic coupling. This cooperative effect facilitated the modulation of the electronic structure and promoted charge separation, improving the electrical responsiveness and surface catalytic activity of $\text{Bi}_4\text{O}_5\text{Br}_2$.

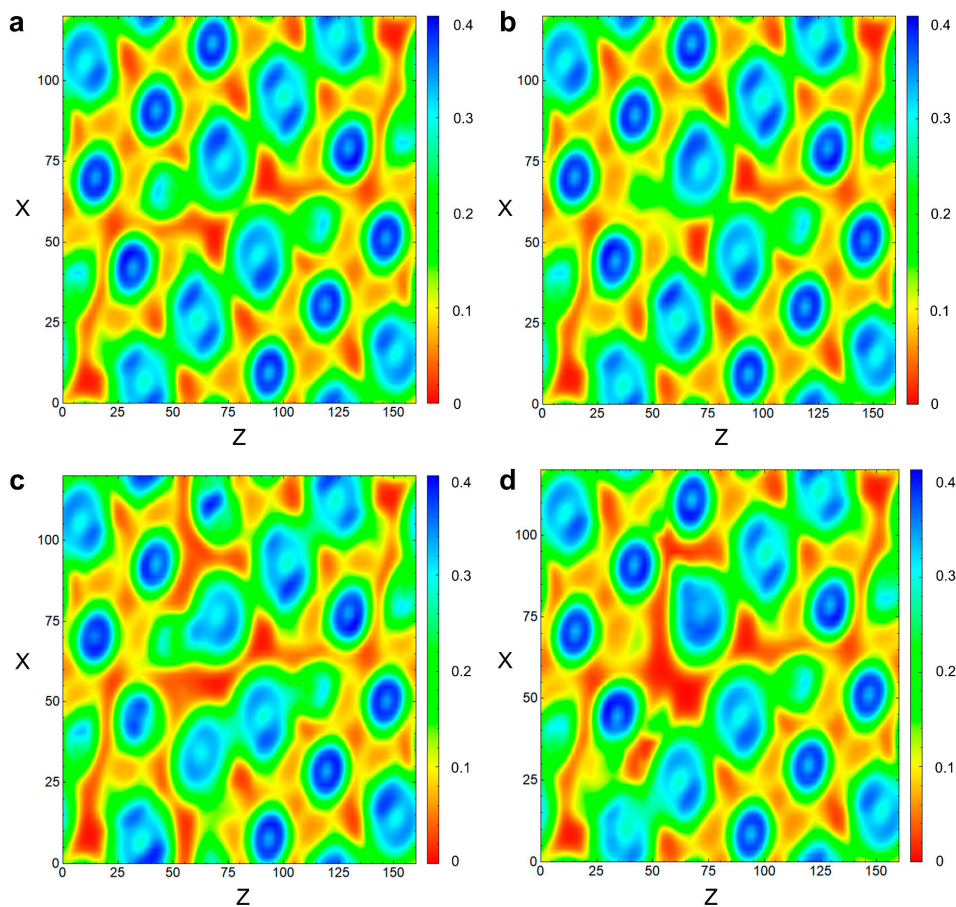


Figure 3. Electron localization function (ELF) of (a) $\text{Bi}_4\text{O}_5\text{Br}_2$, (b) Vo-BOB, (c) Fe-BOB, and (d) Fe-Vo-BOB.

3.3. Energy Band Structure

As illustrated in Figure 4, the spin-polarized band structures of pristine $\text{Bi}_4\text{O}_5\text{Br}_2$ (BOB), the oxygen vacancy-doped system (Vo-BOB), the Fe-doped system (Fe-BOB), and the Fe-doped with oxygen vacancy synergy (Fe-Vo-BOB) were presented, with the Fermi level (E_f) aligned at 0 eV for energy referencing. In Figure 4a,b, the valence band maximum (VBM) of pristine $\text{Bi}_4\text{O}_5\text{Br}_2$ was positioned at the Y point, whereas the conduction band minimum (CBM) occurred at the Γ point. This spatial separation of the band extrema in the Brillouin zone confirmed that $\text{Bi}_4\text{O}_5\text{Br}_2$ is an indirect bandgap semiconductor. Using PBE, pristine $\text{Bi}_4\text{O}_5\text{Br}_2$ shows an indirect band gap of 2.57 eV, consistent with reported experimental values ranging from 2.18 to 2.75 eV [43–51] and theoretical calculations between 2.15 and 2.64 eV [25–27,29,52] (Figure 4a,b; Table S1). Additionally, we compared our results with the experimentally measured and theoretically predicted band gaps of $\text{Bi}_4\text{O}_5\text{Br}_2$ reported in the literature (Table S1). For VO-BOB, the spin-up and spin-down electronic structures are nearly identical, suggesting a closed-shell defect configuration, which is consistent with a doubly occupied neutral oxygen vacancy (F center, Vo^0). Upon introducing oxygen vacancies, distinct impurity levels appeared near the Fermi level (approximately within the –1 to 0 eV region, as seen in Figure 4c,d). This new energy level effectively lowered the energy barrier for electron transitions originating from the valence band to the CBM, consequently reducing the optical bandgap of $\text{Bi}_4\text{O}_5\text{Br}_2$. The introduction of oxygen vacancies disrupted the local electronic structure, inducing the transition of partial valence band electrons to the defect energy level, significantly enhancing the localization of electrons [19,53]. Furthermore, the slight upward shift in the valence band top indicated that the presence of oxygen vacancies elevated the energy level of valence band electrons, reducing the probability of electron-hole recombination. From the perspective of band structure, these results further confirm that oxygen vacancies played a crucial role in enhancing the photoelectronic response and photocatalytic activity of $\text{Bi}_4\text{O}_5\text{Br}_2$.

Further examination of the Fe-doped system (Fe-BOB) revealed pronounced asymmetry between the spin-up and spin-down channels, indicating that Fe doping induced a significant spin polarization effect. As illustrated in Figure 4e,f, the bandgap dramatically decreased to approximately 2.24 eV in the spin-up channel and to about 1.51 eV in the spin-down channel, suggesting that Fe 3d states introduced impurity levels within the forbidden gap, altering the positions of the band edges. This modification not only diminished the transition barrier for electrons from the valence band to the conduction band—boosting the visible-light absorption capability of $\text{Bi}_4\text{O}_5\text{Br}_2$ —but also created additional electronic transport channels through the Fe 3d states, which ensured the efficient separation and migration of photogenerated charge carriers [54]. As shown in Figure 4g,h, when Fe doping coexisted with oxygen vacancies (Fe-Vo-BOB), the band structure underwent more pronounced changes. An increased number of impurity states appeared near the Fermi level, and the bandgap further narrowed, indicating a strong synergistic interaction between Fe doping and oxygen vacancies. The strong coupling between Fe 3d orbitals and defect-induced localized states formed a continuous energy-level bridge between the defect regions and the metal centers, markedly enhancing carrier transport and light absorption. This synergistic effect optimized the electronic structure of $\text{Bi}_4\text{O}_5\text{Br}_2$ and provided more favorable electronic excitation and transfer pathways for photocatalytic CO_2 reduction reactions.

In summary, from the pristine system to the doped, defective, and synergistically modified systems, the electronic structure of $\text{Bi}_4\text{O}_5\text{Br}_2$ was significantly regulated and optimized. Specifically, Fe doping generated 3d impurity levels that enhanced visible-light absorption and facilitated the separation and migration of photogenerated carriers, while oxygen vacancies provided electron-trapping and activation sites that further

improved charge transport. The synergistic interaction between Fe doping and oxygen vacancies resulted in stronger electronic coupling and more favorable band structure modulation, providing a solid theoretical basis for improving the photocatalytic activity and CO₂ reduction kinetics of Bi₄O₅Br₂.

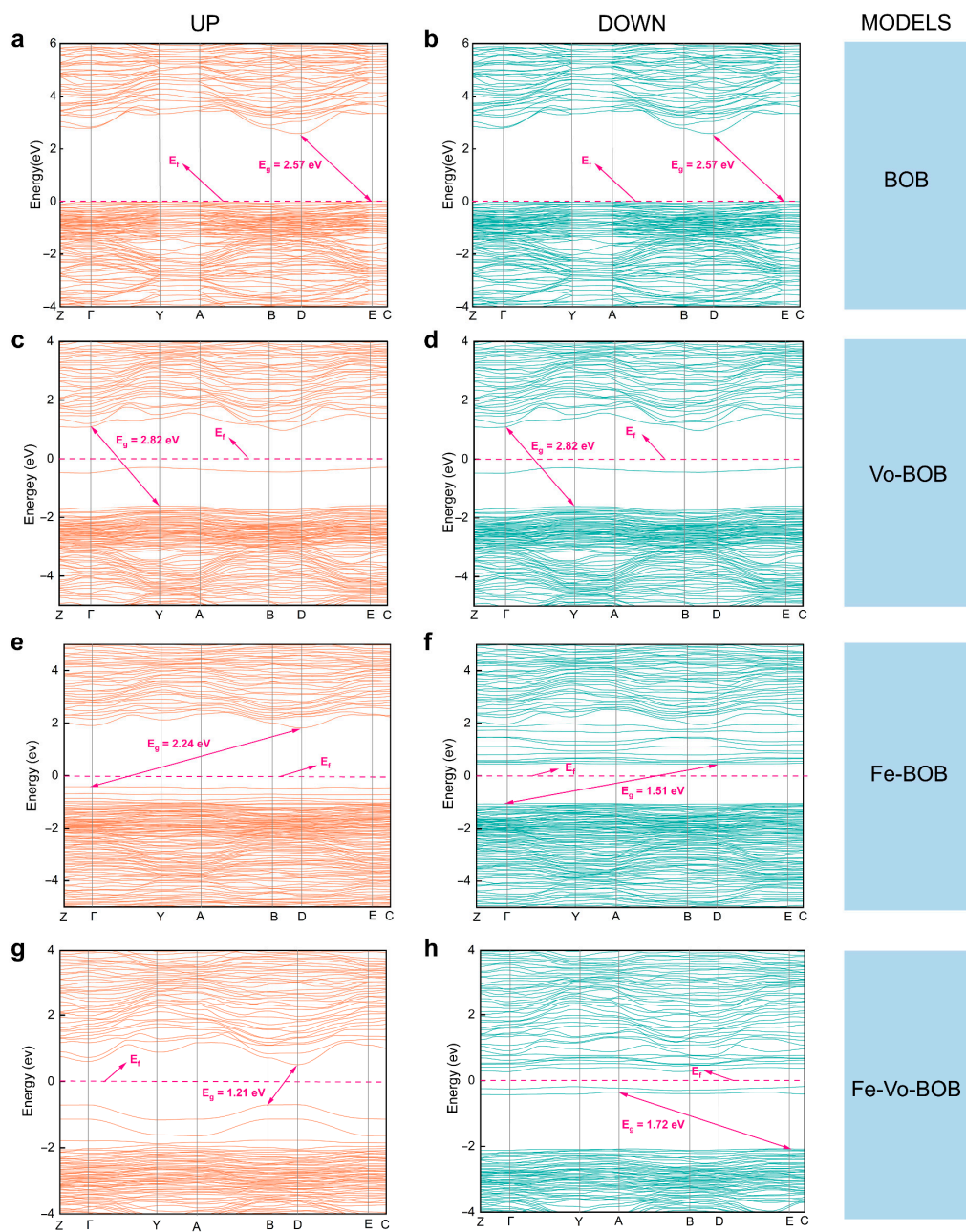


Figure 4. Energy band diagrams of (a) BOB-up, (b) BOB-down, (c) Vo-BOB-up, (d) Vo-BOB-down, (e) Fe-BOB-up, (f) Fe-BOB-down, (g) Fe-Vo-BOB-up, and (h) Fe-Vo-BOB-down.

3.4. Density of States

Figure 5 compares the density of states (DOS) of pristine $\text{Bi}_4\text{O}_5\text{Br}_2$ and its variants modified by oxygen vacancies, Fe doping, and their synergistic regulation. As illustrated in Figure 5a, the upper valence band of pristine $\text{Bi}_4\text{O}_5\text{Br}_2$ was mainly composed of O $2p$ and Br $4p$ orbitals, with a small contribution from Bi $6p$ states. The lower valence band was dominated by Bi $6s$ orbitals, while the conduction band was primarily formed by Bi $6p$ and O $2p$ states.

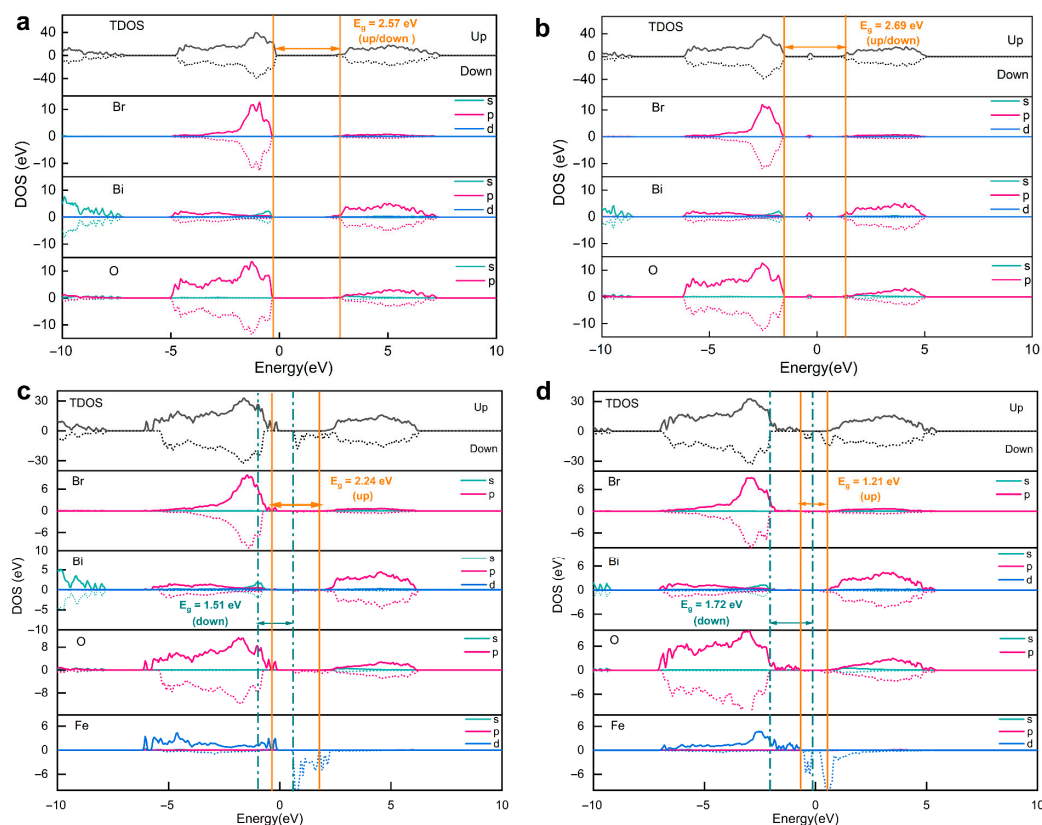


Figure 5. Density of states plots for (a) BOB, (b) Vo-BOB, (c) Fe-BOB, and (d) Fe-Vo-BOB.

After introducing oxygen vacancies (Figure 5b), new defect states appeared near the Fermi level, originating mainly from Bi $6p$ and partly from O $2p$ orbitals. The emergence of these impurity levels suggested that oxygen vacancies facilitated electronic transitions from the valence band maximum to the conduction band minimum, enhancing the excitation and separation of photogenerated carriers and improving the photoelectronic performance of $\text{Bi}_4\text{O}_5\text{Br}_2$ [55].

As shown in Figure 5c, the DOS of Fe-BOB exhibited a pronounced asymmetry between the spin-up and spin-down channels, indicating a strong spin-polarization effect induced by Fe doping. The Fe $3d$ orbitals introduced distinct impurity levels near the Fermi level, significantly increasing the DOS and providing additional electronic transition pathways. The localized Fe $3d$ states near the Fermi level show a local magnetic moment of $3.93 \mu_B$, and the spin-polarization ratio between the up and down spin channels is approximately 2.1. This indicates strong spin polarization around Fe atoms and a significant modification of the electronic structure. The increase in DOS due to Fe $3d$ orbitals near the Fermi level is approximately 0.45 eV for the spin-up channel and 0.25 eV for the spin-down channel.

In the Fe–Vo–BOB system (Figure 5d), a more pronounced spin asymmetry was observed, confirming strong spin polarization. The upper valence band was chiefly composed of O 2*p*, Br 4*p*, and Fe 3*d* states, whereas the conduction band mainly derived from Bi 6*p* and O 2*p* orbitals. The localized Fe 3*d* states near the Fermi level strongly hybridized with O 2*p* orbitals, leading to an enhanced DOS at the conduction band edge. The local magnetic moment of Fe is 3.93 μ_B , and the spin-polarization ratio between the spin-up and spin-down channels is 2.3, indicating significant spin-polarized charge transfer and enhanced magnetic behavior. The excess electrons introduced by oxygen vacancies further promoted the formation and occupation of impurity states. These results were consistent with the band structure analysis, confirming the critical role of the synergistic doping–defect strategy in optimizing the photoelectronic properties of Bi₄O₅Br₂.

3.5. Absorption Spectrum and Dielectric Function

As shown in Figure 6a,b, the UV-vis absorption characteristics of Bi₄O₅Br₂ and its modified systems (Vo–BOB, Fe–BOB, Fe–Vo–BOB) were analyzed. Compared to pristine BOB, both Fe-doping and oxygen vacancies induced a significant red shift in the absorption edge along with enhanced visible-light absorption intensity. This suggests that the introduction of Fe 3*d* orbitals and oxygen vacancies effectively modulates the band structure, improving Bi₄O₅Br₂'s response to low-energy photons and making it more efficient for visible-light-driven photocatalysis. The Vo–BOB system introduced shallow defect states in the band gap, promoting near-edge electronic excitation and stronger absorption in the low-energy region. Notably, the Fe-doped and Fe–Vo co-modified systems showed the strongest absorption across the entire visible-light region, highlighting the synergistic effect between Fe doping and oxygen vacancies. The Tauc extrapolation method (Figure 6b) revealed that the optical band gaps of BOB, Vo–BOB, Fe–BOB, and Fe–Vo–BOB were 2.56 eV, 1.2 eV, 1.51 eV, and 1.25 eV, respectively, indicating that both oxygen vacancies and Fe doping significantly narrow the band gap, with Fe–Vo–BOB showing the smallest band gap of 1.25 eV [56,57]. These modifications not only enhanced light absorption but also improved charge separation, suggesting that the Fe–Vo co-modification offers a promising strategy for enhancing photocatalytic CO₂ reduction under visible light.

The dielectric function analysis shown in Figure 6c,d provides insights into the optical properties of Bi₄O₅Br₂ and its modified systems. Compared with the original BOB (black curve), Vo–BOB (red curve) and Fe–BOB (orange curve) exhibit enhanced responses in the low-energy and middle-energy regions, respectively. The Vo–BOB system shows a clear peak at approximately 1.5 electron volts, mainly due to the electron transitions from the O 2*p* and Bi 6*p* orbitals of the impurity levels to the conduction band bottom. This indicates that the introduction of oxygen vacancies creates shallow defect states within the band gap, promoting electron excitation and enhancing light absorption in the visible light region. In the Fe–BOB system, the Fe doping introduces new Fe 3*d* states, resulting in a wider dielectric response, especially in the middle energy region, and promoting charge transfer and enhanced optical response. The Fe–Vo–BOB system (green curve) shows the most significant improvement, exhibiting enhanced absorption throughout the visible light range. This indicates that the synergistic effect of iron doping and oxygen vacancies not only optimizes the polarization properties of the material but also significantly enhances its ability to absorb light, making it extremely outstanding in visible light-driven photocatalytic applications. This analysis shows that Fe–Vo–BOB provides the best overall optical performance for photocatalytic applications due to the synergistic effect of iron doping and oxygen vacancies. This is consistent with the experimental results of Wu et al. [34], where iron elements and oxygen vacancies were

introduced into bismuth-based materials (such as BiOCl and BiOBr), which have been proven to significantly alter the electronic structure, enhance light absorption capacity, and promote charge separation.

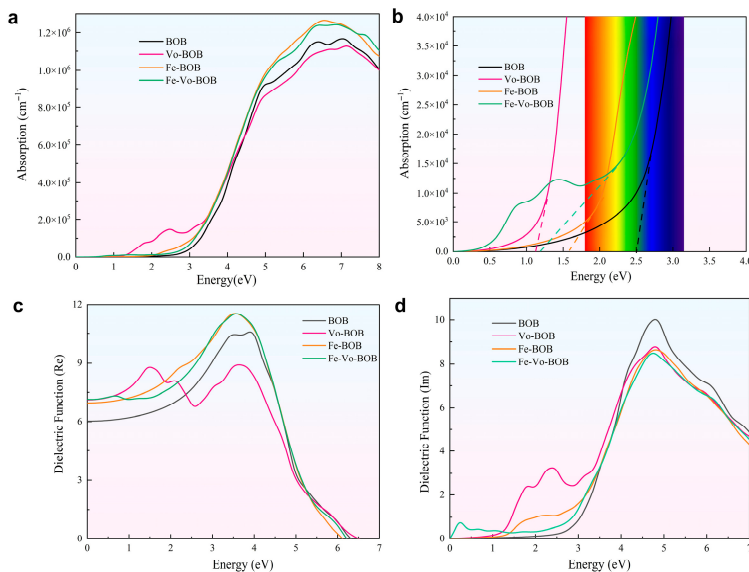
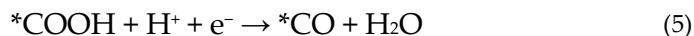
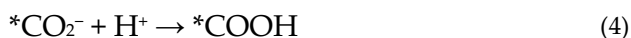


Figure 6. (a) Absorption spectrum and (b) localized magnification in the visible light range for BOB, Vo-BOB, Fe-BOB, and Fe-Vo-BOB. (c) Real part and (d) imaginary part of the dielectric function for BOB, Vo-BOB, Fe-BOB, and Fe-Vo-BOB.

3.6. Photocatalytic CO_2 Reduction

The photocatalytic reduction of CO_2 fundamentally depends on the catalyst's capacity to harvest solar energy and produce photogenerated electrons and holes, which subsequently participate in converting CO_2 to CO on the catalyst surface. This process generally involves several key steps: (i) CO_2 molecules are first adsorbed onto the catalyst surface, establishing the necessary conditions for the reaction; (ii) upon light absorption, electrons in the valence band are excited to the conduction band, generating electron-hole pairs; (iii) the generated charge carriers are then separated and migrate to active sites on the catalyst surface; (iv) under light irradiation, some charge carriers may recombine, while others participate in the CO_2 reduction reaction; and (v) photogenerated electrons react with the adsorbed CO_2 molecules, yielding the target CO product. During the conversion of CO_2 to CO, the specific reaction pathway and the formation of intermediates are determined by the nature of the surface-active sites of the catalyst, with the overall reduction process generally proceeding through multiple elementary steps. The primary elementary reactions involved in the reduction of CO_2 to CO are as follows [42]



To thoroughly understand the synergistic impact of Fe doping and oxygen vacancies on the photocatalytic CO₂ reduction performance of Bi₄O₅Br₂, density functional theory (DFT) calculations were performed to assess the Gibbs free energy changes (ΔG) of the key intermediates (*CO₂, *COOH, and *CO) involved in the CO₂ reduction pathway. By constructing Gibbs free energy profiles, the CO₂ reduction pathways over pristine BOB, oxygen-vacancy-modified BOB (Vo-BOB), Fe-doped BOB (Fe-BOB), and Fe-Vo co-modified BOB (Fe-Vo-BOB) surfaces were systematically compared, providing theoretical insights into the thermodynamic mechanisms underlying the enhanced reactivity and selectivity induced by the synergistic regulation of Fe doping and oxygen vacancies.

The structural models shown in Figure 7 correspond to the fully relaxed adsorption/intermediate states on the same (020) slab with the same surface setup (termination/thickness/vacuum) and the same adsorbate loading (one CO₂ per periodic surface cell) for all BOB-derived models. As shown in Figure 7a, the pristine BOB system exhibits the highest free energy barrier of 2.834 eV at the COOH formation step, which serves as the rate-determining step (RDS) of the overall reaction. This indicates that CO₂ activation and the associated proton-electron coupling are thermodynamically unfavorable in the pristine system. The high energy barrier for COOH formation suggests that the material is inefficient at stabilizing intermediates and promoting CO₂ activation.

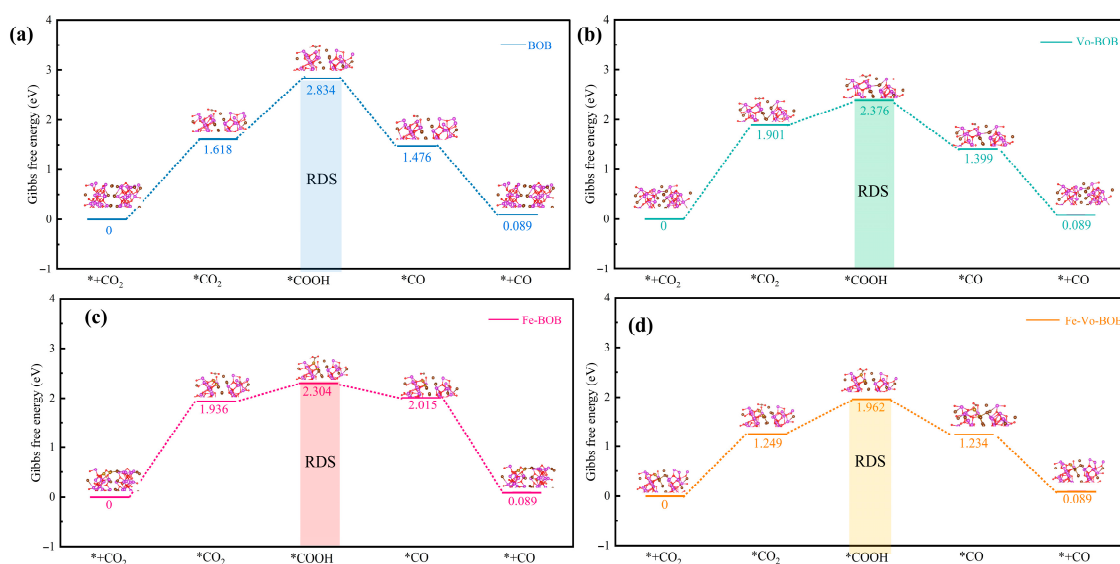


Figure 7. Pathways and activation energies of (a) BOB, (b) Vo-BOB, (c) Fe-BOB, and (d) Fe-Vo-BOB in the CO₂ reduction reaction.

As shown in Figure 7b, after introducing Vo-BOB, the energy barriers for COOH and CO intermediates decrease significantly to 2.376 eV and 1.399 eV, respectively, compared to the pristine BOB system. This indicates that oxygen vacancies facilitate electron accumulation, enhancing CO₂ adsorption and activation. The marked reduction in the energy barriers suggests that oxygen vacancies contribute to more effective electron donation and stabilization of intermediates, thereby providing a more favorable reaction pathway for CO₂ reduction.

In the Fe-BOB, as shown in Figure 7c, the energy barrier for the COOH intermediate further decreases to 2.304 eV, indicating that the Fe 3d orbitals provide additional electronic channels that hybridize with CO₂ molecular orbitals, promoting charge transfer and stabilizing the reaction intermediates. The introduction of Fe doping aids in

facilitating electron transfer and stabilizing the intermediates, thereby lowering the overall energy barrier for CO₂ activation [58].

Notably, the Fe–Vo–BOB system, as shown in Figure 7d, exhibits the lowest overall energy barriers. The RDS for CO₂ reduction is reduced to 1.249 eV at the CO₂ adsorption step, with the COOH intermediate stabilized at 1.962 eV. The CO formation step becomes an exergonic reaction with a value of 1.234 eV, indicating that the entire reaction pathway is energetically favorable. Mechanistically, oxygen vacancies enhance charge localization and CO desorption, while Fe doping introduces 3*d* states, promoting electron transfer and stabilizing the reaction intermediates. The synergistic effect between the two forms a continuous energy bridge between the defect regions and metal centers, optimizing the reaction pathway, enhancing the migration efficiency of photo-generated electrons, and effectively promoting CO₂ conversion to CO [59].

4. Conclusions

This study involved carrying out first-principles calculations to systematically explore the synergistic effects of iron (Fe) doping and oxygen vacancies on the structural, electronic and optical properties of bismuth (IV) oxide (Bi₄O₅Br₂), as well as its photocatalytic CO₂ reduction mechanism. The results demonstrated that the Fe-doped, oxygen-defective, and Fe–Vo co-modified Bi₄O₅Br₂ systems possess excellent thermodynamic and dynamic stability, confirming their structural reliability under realistic operating conditions. The introduction of oxygen vacancies generates defect levels near the Fermi level, effectively narrowing the band gap, enhancing charge localization, and improving CO₂ adsorption and activation capability. Meanwhile, Fe doping induces strong spin polarization and introduces Fe 3*d* impurity states that couple efficiently with O 2*p* orbitals, leading to improved charge-carrier transport, enhanced electronic conductivity, and increased visible-light absorption. When both Fe dopants and oxygen vacancies coexist, a remarkable synergistic interaction occurs, forming a continuous energy-level bridge between Fe 3*d* states and defect-induced localized states. This strong electronic coupling substantially improves charge separation efficiency, extends light-harvesting capacity into the visible and near-infrared regions, and optimizes dielectric polarization, collectively boosting the efficiency of light-to-energy conversion. Gibbs free energy analyses further revealed that the Fe–Vo–BOB system exhibits the lowest reaction energy barriers and the most favorable thermodynamic pathway for CO₂ adsorption, activation, and subsequent conversion into CO, highlighting its superior photocatalytic reactivity compared to the singly modified systems. Overall, the cooperative regulation of Fe doping and oxygen vacancy engineering effectively tailors the band structure and charge transfer dynamics of Bi₄O₅Br₂, resulting in improved optical properties and heightened photocatalytic CO₂ reduction performance. These results offer important theoretical guidance for the rational design of high-performance photocatalysts co-modulated by defects and dopants, and provide key insights for developing next-generation visible-light-driven catalysts for solar-to-chemical energy conversion and environmental remediation. In summary, the main advance of this work is the explicit identification of a nearest-neighbor Fe–Vo coupled defect in Bi₄O₅Br₂ and the demonstration of its synergistic mechanism through a consistent comparison of pristine, Fe-only, Vo-only, and Fe–Vo models. This coupled defect exhibits a more favorable electronic/optical response and improves the CO₂ → CO reaction energetics compared with single-dopant cases, thereby advancing beyond prior Ni/Mn/Co doping and earlier Fe-doping descriptions that did not explicitly address dopant–vacancy coupling.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/magnetochemistry12020026/s1>, Table S1: Comparison of Experimental and Theoretical Band Gaps of Bi₄O₅Br₂; Table S2: AIMD settings and quantitative stability metrics.

Author Contributions: Conceptualization, F.Z.; formal analysis, X.H. and H.S.; methodology, X.Y. and N.D.; visualization, G.L. and S.L.; writing—original draft, G.L.; writing—review and editing, F.Z. and S.X. All authors have read and agreed to the published version of the manuscript.

Funding: This work was funded by the National Natural Science Foundation of China (62264015) and Shaanxi Provincial Department of Education (Grant No. 22JK0623).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The original contributions presented in this study are included in the article/Supplementary Materials. Further inquiries can be directed to the corresponding authors.

Acknowledgments: G.H Liu was partially supported by the postgraduate research opportunities program of HZWTECH (HZWTECH-PROP).

Conflicts of Interest: The authors declare no conflicts of interest.

Reference

1. Sun, L.; Zhang, Z.; Bian, J.; Bai, F.; Su, H.; Li, Z.; Xie, J.; Xu, R.; Sun, J.; Bai, L.; et al. A Z-scheme heterojunctional photocatalyst engineered with spatially separated dual redox sites for selective CO₂ reduction with water: Insight by in situ μ s-transient absorption spectra. *Adv. Mater.* **2023**, *35*, 2300064.
2. Pan, W.; Wei, Z.; Su, Y.; Lian, Y.; Zheng, Z.; Yuan, H.; Qin, Y.; Xie, X.; Bai, Q.; Jiao, Z.; et al. Hydroxylated metal-organic-layer nanocages anchoring single atomic cobalt sites for robust photocatalytic CO₂ reduction. *Nano Res.* **2024**, *17*, 2410–2419.
3. Wu, J.; Zhu, J.; Fan, W.; He, D.; Hu, Q.; Zhu, S.; Yan, W.; Hu, J.; Zhu, J.; Chen, Q.; et al. Selective photoreduction of CO₂ to CH₄ triggered by metal-vacancy pair sites. *Nano Lett.* **2024**, *24*, 696–702.
4. Li, X.; Wang, M.; Wang, R.; Wang, Y.; Zhu, M.; Zhang, L.; Shi, J.; Construction of Ru single-atoms on ceria to reform the products of CO₂ photoreduction. *ACS Nano* **2024**, *18*, 5741–5751.
5. Dong, J.; Zhao, J.; Yan, X.; Li, L.; Liu, G.; Ji, M.; Wang, B.; She, Y.; Li, H.; Xia, J. Construction of carbonized polymer dots/potassium doped carbon nitride nanosheets van der Waals heterojunction by ball milling method for facilitating photocatalytic CO₂ reduction performance in pure water. *Appl. Catal. B* **2024**, *351*, 123993.
6. Wang, Y.; Yan, Y.; Zhang, H.; Peng, X.; Huang, H.; Zhang, S.; Shi, L. Stabilizing electron-rich Ni single-atoms on black phosphorus nanosheets boosts photocatalytic carbon dioxide reduction. *J. Colloid Interface Sci.* **2024**, *658*, 324–333.
7. Chen, Z.; Jin, X.; Lan, Q.; Li, X.; Huang, Q.; Liu, W.; Guo, Y.; Xie, H.; Ye, L. Achieving high carrier separation over Bi₄O₅I₂ through Ni doping for improved photocatalytic CO₂ reduction. *Nanotechnology* **2023**, *34*, 405201.
8. Li, C.; Lu, X.; Chen, L.; Xie, X.; Qin, Z.; Ji, H.; Su, T. WO₃/BiOBr S-scheme heterojunction photocatalyst for enhanced photocatalytic CO₂ reduction. *Materials* **2024**, *17*, 3199.
9. Lin, H.; Li, X.; Cao, J.; Chen, S.; Chen, Y. Novel I[−]-doped BiOBr composites: Modulated valence bands and largely enhanced visible light phtotocatalytic activities. *Catal. Commun.* **2014**, *49*, 87–91.
10. Shang, J.; Hao, W.C.; Lv, X.J.; Wang, T.; Wang, X.; Du, Y.; Dou, S.; Xie, T.; Wang, D.; Wang, J. Bismuth oxybromide with reasonable photocatalytic reduction activity under visible light. *ACS Catal.* **2014**, *4*, 954–961.
11. Kato, D.; Hongo, K.; Maezono, R. Valence band engineering of layered bismuth oxyhalides toward stable visible-light water splitting: Madelung site potential analysis. *J. Am. Chem. Soc.* **2017**, *139*, 18725–18731.
12. Wang, X.; Zhang, Y.; Miao, W.; Zhang, X.; Shi, Y.; Tang, Z.; Shi, H. Insight into the pathway, improvement of performance and photocatalytic mechanism of active carbon/Bi₄O₅Br₂ composite for cefixime and rhodamine B removal. *J. Photoch. Photobio. A* **2023**, *444*, 114892.
13. Zhang, Z. Construction and Photocatalytic Degradation Performance of Bi₄O₅Br₂-Based Heterojunction Photocatalysts. Master's Thesis, South China University of Technology, Guangzhou, China, 2022. (In Chinese)

14. Lu, S.; Li, J.; Duan, F.; Duan, L.; Du, M.; Chen, M. One-step preparation of $\text{Bi}_4\text{O}_5\text{Br}_{1-x}\text{I}_x$ solid solution with superior photocatalytic performance for organic pollutants degradation under visible light. *Appl. Surf. Sci.* **2019**, *475*, 577–586.
15. Di, J.; Ji, M.; Xia, J.; Li, X.; Fan, W.; Zhang, Q.; Li, H. $\text{Bi}_4\text{O}_5\text{Br}_2$ ultrasmall nanosheets in situ strong coupling to MWCNT and improved photocatalytic activity for tetracycline hydrochloride degradation. *J. Mol. Catal. A-Chem.* **2016**, *424*, 331–341.
16. Qian, X.; Ma, Y.; Xia, X.; Xia, J.; Ye, J.; He, G.; Chen, H. Recent progress on $\text{Bi}_4\text{O}_5\text{Br}_2$ -based photocatalysts for environmental remediation and energy conversion. *Catal. Sci. Technol.* **2024**, *14*, 1085–1104.
17. Zhang, L.; Li, Y.; Li, Q.; Fan, J.; Carabineiro, S.A.C.; Lv, K. Recent advances on bismuth-based photocatalysts: Strategies and mechanisms. *Chem. Eng. J.* **2021**, *419*, 129484.
18. Wang, Q.; Liu, Z.; Liu, D.; Liu, G.; Yang, M.; Cui, F.; Wang, W. Ultrathin two-dimensional $\text{BiOBr}_{1-x}\text{I}_x$ solid solution with rich oxygen vacancies for enhanced visible-light-driven photoactivity in environmental remediation. *Appl. Catal. B* **2018**, *236*, 222–232.
19. Mao, D.; Hu, Y.; Yang, S.; Liang, J.; He, H.; Yang, S.; Xu, Z.; Sun, C.; Zeng, S.; Jiang, Z.; et al. Oxygen-vacancy-induced charge localization and atomic site activation in ultrathin $\text{Bi}_4\text{O}_5\text{Br}_2$ nanotubes for boosted CO_2 photoreduction. *Chem. Eng. J.* **2022**, *452*, 139304.
20. Jiang, Z.; Xiao, C.; Yin, X.; Xu, L.; Liu, C.; Wang, H. Facile preparation of a novel $\text{Bi}_{24}\text{O}_{31}\text{Br}_{10}$ /nano-ZnO composite photocatalyst with enhanced visible light photocatalytic ability. *Ceram. Int.* **2020**, *46*, 10771–10778.
21. Popov, A.; Koto, E.; Kuklja, M. Quantum Chemical Calculations of the Electron Center Diffusion in MgO Crystals. *Phys. Status Solidi* **1996**, *195*, 61.
22. Lushchik, A.; Podelinska, A.; Seeman, V.; Shablonin, E.; Kotomin, E.; Kuzovkov, V. Open Questions on the Thermal Stability of Primary Electronic Centers in Irradiated MgO Single Crystals. *J. Phys. Chem. C* **2025**, *129*, 2775–2781.
23. Di, J.; Xia, J.; Chisholm, M.F.; Zhong, J.; Chen, C.; Cao, X.; Dong, F.; Chi, Z.; Chen, H.; Weng, X.; et al. Defect-tailoring mediated electron-hole separation in single-unit-cell $\text{Bi}_3\text{O}_4\text{Br}$ nanosheets for boosting photocatalytic hydrogen evolution and nitrogen fixation. *Adv. Mater.* **2019**, *31*, 1807576.
24. Zhang, W.; Zhu, G.; Yang, W.; Sun, Q.; Wu, Q.; Tian, Y.; Zhang, Z.; Zhang, S.; Cheng, S.; Zhang, C.; et al. Fe-doped $\text{Bi}_4\text{O}_5\text{Br}_2$ visible light photocatalyst: A first principles investigation. *J. Theor. Comput. Chem.* **2018**, *17*, 1850031.
25. Zhu, G.; Hojamberdiev, M.; Zhang, W.; Taj Ud Din, S.; Joong Kim, Y.; Lee, J. Yang, W. Enhanced photocatalytic activity of Fe-doped $\text{Bi}_4\text{O}_5\text{Br}_2$ nanosheets decorated with Au nanoparticles for pollutants removal. *Appl. Surf. Sci.* **2020**, *526*, 146760.
26. Zhang, W.; Xiao, X.; Wu, Q.; Fan, Q.; Chen, S.; Yang, W.; Zhang, F. Facile synthesis of novel Mn-doped $\text{Bi}_4\text{O}_5\text{Br}_2$ for enhanced photocatalytic NO removal activity. *J. Colloid Interface Sci.* **2020**, *826*, 154204.
27. Zhang, W.; Chen, S.; He, M.; Zhu, G.; Yang, W.; Tian, Y.; Zhang, Z.; Zhang, S.; Zhang, F.; Wu, Q. Enhanced photocatalytic properties of $\text{Bi}_4\text{O}_5\text{Br}_2$ by Mn doping: A first principles study. *Mater. Res. Express* **2018**, *5*, 075512.
28. Yang, Z.; Hu, B.; Wang, X.; Selishchev, D.; Zhang, G. Enhanced photocatalytic CO_2 reduction over Ni-doped $\text{Bi}_4\text{O}_5\text{Br}_2/\text{NiCo}_2\text{O}_4$ heterojunction: Synergistic enhancement effect between spin polarization and built-in electric field. *ACS Sustain. Chem. Eng.* **2025**, *13*, 1095–1105.
29. Sheng, H.; Zhang, X.; Xin, S.; Shi, H.; Liu, G.; Wu, Q.; Xue, S.; Wang, X.; Shao, T.; Liu, Y.; et al. First-principles study of electronic structure and optical properties of Ni-doped $\text{Bi}_4\text{O}_5\text{Br}_2$. *Coatings* **2024**, *14*, 67.
30. Wu, H.; Liu, X.; Xu, H.; Yang, X.; Ye, J. Efficient photodegradation of 2-chloro-4-nitrophenol over Fe-doped BiOCl nanosheets with oxygen vacancy. *Catal. Sci. Technol.* **2021**, *11*, 5119.
31. Wang, Y.; Ban, C.; Meng, J.; Ma, J.; Zou, H.; Feng, Y.; Ding, J.; Duan, Y.; Gan, L.; Zhou, X. Charge localization induced by Fe doping in porous Bi_2O_3 Micro-flower for enhanced photoreduction of CO_2 to CO. *Sep. Purif. Technol.* **2023**, *312*, 123379.
32. Blöchl, P.E. Projector augmented-wave method. *Phys. Rev. B* **1994**, *50*, 17953.
33. Grimme, S. Semiempirical GGA-type density functional constructed with a long range dispersion correction. *J. Comput. Chem.* **2006**, *27*, 1787–1799.
34. Perdew, J.P.; Burke, K.; Ernzerhof, M. Generalized gradient approximation made simple. *Phys. Rev. Lett.* **1996**, *77*, 3865–3868.
35. Shih, Y.; Sergienko, A.; Rubin, M.; Kiess, T.; Alley, C. Two-photon entanglement in type-II parametric down-conversion. *Phys. Rev. B* **1994**, *50*, 23.
36. An, W.; Wang, H.; Yang, T.; Xu, J.; Wang, Y.; Liu, D.; Hu, J.; Cui, W.; Liang, Y. Enriched photocatalysis-Fenton synergistic degradation of organic pollutants and coking wastewater via surface oxygen vacancies over Fe- BiOBr composites. *Chem. Eng. J.* **2023**, *451*, 138653.

37. Liu, G.; Dai, R.; Shi, H.; Dong, N.; Zhang, B.; Li, S.; Wang, W.; Liu, Y.; Shao, T.; Zhang, M.; et al. Using Er/Cd-Co doped Bi₄O₅Br₂ microspheres to enhance antibiotic degradation under visible illumination: A combined experimental and DFT investigation. *J. Phys. Chem. B* **2024**, *128*, 9373–9384.
38. Dai, R. Preparation of Metal Ion-Doped Bi₄O₅Br₂ Materials and Investigation of Their Photocatalytic Properties. Master's Thesis, Yan'an University, Yan'an, China, 2022. (In Chinese)
39. Liu, G.; Shi, H.; Dong, N.; Cao, X.; Gao, X.; Xue, S.; Zhang, F. First-principles exploration of the electronic structure and optical properties of S-doped Bi₄O₅Br₂. *Catalysts* **2025**, *15*, 228.
40. Zhang, Q.; Wang, X.; Zhang, F.; Fang, C.; Liu, D.; Zhou, Q. A High-throughput screening toward efficient nitrogen fixation: Transition metal single-atom catalysts anchored on an emerging π - π conjugated graphitic carbon nitride (g-C₁₀N₃) substrate with dirac dispersion. *ACS Appl. Mater. Interfaces* **2023**, *15*, 11812–11826.
41. Jacques, K.; Desmarais, G.V.; Bencheikh, K.; Erba, A.; Pittalis, S. Electron localization function for noncollinear spins. *Phys. Rev. Lett.* **2024**, *133*, 136401.
42. Zeng, J.; Jiang, Z.; Lv, K.; Ahmad, S.A.; Chen, X.; Zhang, W.; Xie, J.; Zhu, T. Experimental and calculation investigations of the photocatalytic selective and performance for CO₂ reduction by cobalt-doped Bi₄O₅Br₂ nanosheets. *Ceram. Int.* **2024**, *51*, 1801–1812.
43. Vadivel, S.; Fujii, M.; Rajendran, S. Novel S-scheme 2D/2D Bi₄O₅Br₂ nanoplatelets/g-C₃N₅ heterojunctions with enhanced photocatalytic activity towards organic pollutants removal. *Environ. Res.* **2022**, *213*, 113736.
44. Zhao, C.; Li, X.; Yue, L.; Ren, X.; Yuan, S.; Zeng, Z.; Hu, X.; Wu, Y.; He, Y. Bi₄O₅Br₂ nanoflower and CdWO₄ nanorod heterojunctions for photocatalytic synthesis of ammonia. *ACS Appl. Nano Mater.* **2023**, *6*, 15709–15720.
45. Shi, H.; Wang, W.; Zhang, L.; Tang, Z.; Fan, J. Enhancement of photocatalytic disinfection performance of the Bi₄O₅Br₂ with the modification of silver quantum dots. *J. Environ. Chem. Eng.* **2021**, *9*, 105867.
46. Di, J.; Xia, J.; Ji, M.; Yin, S.; Li, H.; Xu, H.; Zhang, Q.; Li, H. Controllable synthesis of Bi₄O₅Br₂ ultrathin nanosheets for photocatalytic removal of ciprofloxacin and mechanism insight. *J. Mater. Chem. A* **2015**, *3*, 15108.
47. Yang, H. Study on the Preparation and Photocatalytic Performance of Modified Bi₄O₅Br₂. Professional Master's Thesis, Northwest University, Xi'an, China, 2021. (In Chinese)
48. Xia, J.; Ge, Y.; Di, J.; Xu, L.; Yin, S.; Chen, Z.; Liu, P.; Li, H. Ionic liquid-assisted strategy for bismuth-rich bismuth oxybromides nanosheets with superior visible light-driven photocatalytic removal of bisphenol-A. *J. Colloid Interf. Sci.* **2016**, *473*, 112–119.
49. Bai, Y.; Chen, T.; Wang, P.; Wang, L.; Ye, L. Bismuth-rich Bi₄O₅X₂ (X = Br, and I) nanosheets with dominant {1 0 1} facets exposure for photocatalytic H₂ evolution. *Chem. Eng. J.* **2016**, *304*, 454–460.
50. Xiao, X.; Tu, S.; Lu, M.; Zhong, H.; Zheng, C.; Zuo, X.; Nan, J. Discussion on the reaction mechanism of the photocatalytic degradation of organic contaminants from a viewpoint of semiconductor photo-induced electrocatalysis. *Appl. Catal. B-Environ. Energy* **2016**, *198*, 124–132.
51. Guo, Y.; Zhang, W.; Yang, Y.; Wang, C. The photocatalytic efficiency enhancement of Bi₄O₅Br₂ by Li-intercalation for NO removal. *J. Phys. Chem. Solids* **2021**, *159*, 110256.
52. Zhang, J.; Liu, Y.; Xin, S.; Lin, S.; Zhang, X.; Wang, J.; Guo, X.; Zhang, H.; Ramachandran, A.; Ma, H.; Zhang, F.; Zhang, Q.; Liu, X. First-principles study of the effect of Bi content on the photocatalytic performance of bismuth bromide oxide-based catalysts. *Phys. Chem. Phys.* **2025**, *3*, 15108–15118.
53. Zhao, L.; Fang, W.; Meng, X.; Wang, L.; Bai, H.; Li, C. In-situ synthesis of metal Bi to improve the stability of oxygen vacancies and enhance the photocatalytic activity of Bi₄O₅Br₂ in H₂ evolution. *J. Alloys Compd.* **2022**, *910*, 164883.
54. Zhang, L.; Wang, Z.; Li, T.; Hu, C.; Yang, M. Ultrathin Bi₄O₅Br₂ nanosheets with surface oxygen vacancies and strong interaction with Bi₂O₂CO₃ for highly efficient removal of water contaminants. *Environ. Sci.-Nano* **2022**, *9*, 1341.
55. Cao, L.; Zhou, Y.; Gao, L.; Yin, H.; Zhang, M.; Zhang, H.; Ju, P.; Dou, K.; Ai, S. Ascorbic acid induced the improved oxygen vacancy defects of Bi₄O₅Br₂ and its application on photoelectrochemical detection of DNA demethylase MBD₂ with improved detection sensitivity. *Small* **2023**, *20*, 2306365.
56. Qu, S.Y.; Xiong, Y.H.; Zhang, J. Graphene oxide and carbon nanodots co-modified BiOBr nanocomposites with enhanced photocatalytic 4-chlorophenol degradation and mechanism insight. *J. Colloid Interface Sci.* **2018**, *527*, 78–86.
57. Bai, Y.; Shi, X.; Wang, P.Q.; Wang, L.; Zhang, K.; Zhou, Y.; Xie, H.Q.; Wang, J.N.; Ye, L.Q. BiOBr_xI_{1-x}/BiOBr heterostructure engineering for efficient molecular oxygen activation. *Chem. Eng. J* **2018**, *23*, 179–186.

58. Liu, L.; Wang, K.; Zhang, J.; Li, Y.; Li, Y.; Yang, N.; Guo, N. Study on Fe-doped BiOBr with enhanced visible photocatalytic activity for the degradation of levofloxacin. *Mater. Lett.* **2024**, *373*, 137122.
59. Zhang, N.; Li, L.; Shao, Q.; Zhu, T.; Huang, X.; Xiao, X. Fe-Doped BiOCl Nanosheets with Light-Switchable Oxygen Vacancies for Photocatalytic Nitrogen Fixation. *ACS Appl. Energy Mater.* **2019**, *2*, 8394–8398.

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.