

Article

First-Principles Insights into I Doping Effects on the Electronic Structure, Optical Properties, and CO₂ Photoreduction Performance of Bi₄O₅Br₂

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Abstract

To address the insufficient visible-light absorption of Bi₄O₅Br₂ photocatalysts, first-principles density functional theory (DFT) calculations were employed to systematically investigate the effects of I doping at different concentrations (12.5%, 25%, 50%, 75%, 87.5%, and 100%) on the geometric structure, electronic structure, optical properties, and photocatalytic CO₂ reduction performance of Bi₄O₅Br₂. Formation energy calculations and Ab initio molecular dynamics (AIMD) simulations indicate that the I-doped systems possess good thermodynamic and kinetic stability. Geometric analysis shows that I doping leads to a gradual expansion of lattice parameters along the c-axis (from 14.80 Å to 15.16 Å), due to the larger ionic radius of I[−] compared to Br[−]. Electronic structure results reveal that all doped systems remain indirect band gap semiconductors, with the band gap decreasing from 2.56 eV for the pristine system to 2.25 eV at 87.5% doping. This reduction is mainly attributed to the progressive substitution of Br 4p states by I 5p states near the valence band maximum, which modifies the valence band structure. Differential charge density analysis shows electron transfer from Bi to I, enhancing local polarization effects. Optical property calculations demonstrate a pronounced red shift in the absorption edge and significantly enhanced absorption intensity in the visible region after I doping. The real and imaginary parts of the dielectric function also exhibit red shifts and increased peak intensities in the low-energy region. Gibbs free energy analysis indicates that the Gibbs free energy for *COOH formation decreases from 2.83 eV in the pristine system to 2.68 eV after I doping, while the free energy of the *CO intermediate decreases from 1.28 eV to 0.98 eV, significantly improving the CO₂ reduction pathway. This study provides a theoretical basis for improving the optical response and the thermodynamics of the CO₂ reduction reaction through halogen substitution, suggesting a promising strategy for enhancing the photocatalytic potential of Bi₄O₅Br₂.

Keywords: Bi₄O₅Br₂; I doping; first-principles; electronic structure; CO₂ reduction



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1. Introduction

In recent years, global energy shortages and environmental pollution have intensified. In particular, large-scale CO₂ emissions from fossil fuel combustion are widely recognized

as a major contributor to the greenhouse effect [1,2]. Photocatalytic CO₂ reduction has attracted considerable attention because it enables the direct conversion of CO₂ into value-added fuels, such as CO and CH₄ using solar energy. This process is regarded as a promising strategy for achieving carbon neutrality and sustainable development [3–6]. However, most reported photocatalysts suffer from limited visible-light absorption, rapid recombination of photogenerated charge carriers, and high reaction Gibbs free energy, which severely restrict their practical applications [7,8].

Bismuth oxyhalides (BiOX, X = Cl, Br, I) have emerged as an important class of photocatalytic materials due to their unique layered structures, tunable electronic properties, and excellent chemical stability [9,10]. Among them, Bi₄O₅Br₂ is composed of alternating [Bi₂O₂]²⁺ layers and Br₂^{2−} slabs, forming an internal electric field that facilitates charge separation and provides an appropriate response to visible light. As a result, it has demonstrated potential in CO₂ reduction and pollutant degradation [11,12]. Nevertheless, Bi₄O₅Br₂ still exhibits a relatively wide band gap (approximately 2.35–2.56 eV), leading to insufficient utilization of visible light. In addition, the high recombination rate of charge carriers further limits its photocatalytic efficiency [13]. Therefore, it is necessary to develop effective modification strategies to optimize its electronic structure and surface reactivity.

Nonmetal doping is an effective approach to modulate the band structure and optical properties of semiconductors [14]. The incorporation of nonmetal elements such as F, N, and S can introduce impurity states within the band gap, thereby tuning the band gap width and extending the light absorption range [15,16]. Iodine (I), owing to its larger ionic radius and high-energy 5*p* orbitals, can significantly alter the local electronic environment of Bi₄O₅Br₂ when substituting for Br, thereby regulating its band structure and optical properties. Previous experimental studies have shown that I doping induces a red shift in the absorption edge and enhances visible-light-driven photocatalytic degradation activity [17]. In addition, I modification can adjust the conduction band position and improve pollutant removal efficiency [18]. However, systematic theoretical investigations on the concentration-dependent evolution of the electronic structure, the underlying optical response mechanism, and the impact on CO₂ reduction pathways remain limited.

Therefore, in this work, first-principles density functional theory (DFT) calculations were performed to systematically investigate the effects of I doping at different concentrations (12.5%, 25%, 50%, 75%, 87.5%, and 100%) on the crystal structure, electronic structure, optical properties, and Gibbs free energy of CO₂ reduction in Bi₄O₅Br₂. Formation energy and thermal stability, lattice parameter evolution, band structure and density of states, differential charge density, absorption spectra and dielectric function, as well as the Gibbs free energy changes in key intermediates (CO₂, COOH, *CO) along the CO₂ reduction pathway were analyzed. The results reveal the microscopic mechanism by which I substitution regulates the electronic structure, optical response, and thermodynamic characteristics of CO₂ reduction, providing theoretical guidance for the rational design of visible-light-responsive photocatalysts.

2. Results and Discussion

2.1. Formation Energy and Geometric Structure

To evaluate the thermodynamic stability of Bi₄O₅Br₂ with different I doping concentrations, the formation energies of all substituted configurations were calculated. As shown in Figure 1, the minimum formation energy increases progressively with increasing I concentration, with values of 0.558, 1.21, 2.44, 3.66, 4.37, and 4.87 eV for doping levels of 12.5%, 25%, 50%, 75%, 87.5%, and 100%, respectively. Although the formation energy increases at higher doping levels, all systems exhibit positive formation energies.

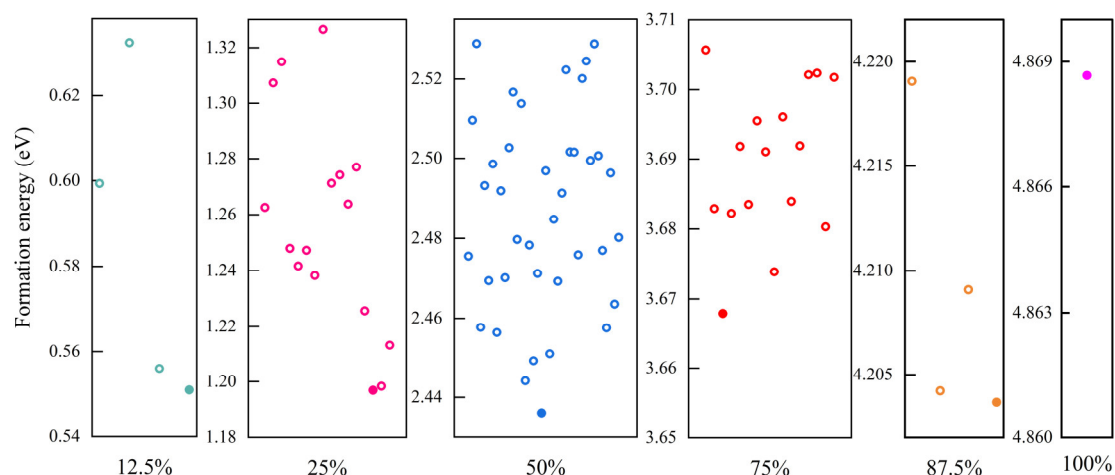


Figure 1. Formation energies of all possible structures of $\text{Bi}_4\text{O}_5\text{Br}_2$ doped with different concentrations of I.

To further assess kinetic stability, ab initio molecular dynamics (AIMD) simulations (300 K, 6 ps) were performed for the configurations with the highest formation energy at each concentration (Figure 2). The results show that all doped systems maintain structural integrity throughout the simulations, with no evidence of bond breaking or structural collapse. The temperature fluctuates slightly around 300 K, and no significant drift in total energy is observed.

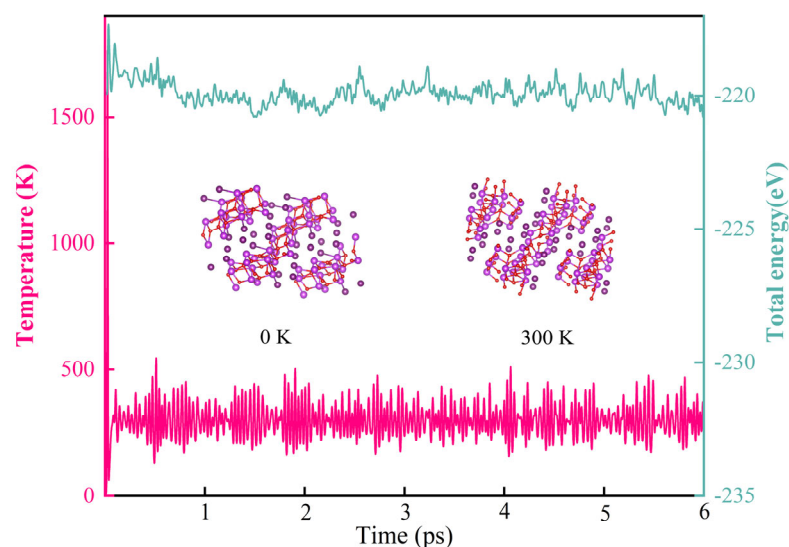


Figure 2. AIMD simulations of I doped $\text{Bi}_4\text{O}_5\text{Br}_2$.

These results indicate that I-substituted $\text{Bi}_4\text{O}_5\text{Br}_2$ systems possess good kinetic stability at finite temperature and can remain structurally stable [19]. Therefore, all subsequent property calculations are based on the configurations with the lowest formation energy at each doping concentration. The corresponding optimized structures are shown in Figure 3.

The optimized lattice parameters are summarized in Table 1. Pristine $\text{Bi}_4\text{O}_5\text{Br}_2$ exhibits lattice constants of $a = 11.10 \text{ \AA}$, $b = 5.74 \text{ \AA}$, $c = 14.80 \text{ \AA}$, and $\beta = 98.38^\circ$. With increasing I substitution levels, all lattice parameters (a , b , and c) show a gradual expansion. Notably, the variation along the c -axis is the most pronounced, with c values of 14.79, 14.87, 14.95, 14.99, 15.18, and 15.16 $\text{\AA}$ for doping levels of 12.5%, 25%, 50%, 75%, 87.5%, and 100%, respectively.

The observed lattice expansion is primarily attributed to the larger ionic radius of I^- (0.216 nm) compared to Br^- (0.195 nm). Substitution of Br by I results in elongation of

Bi-X bonds, particularly along the interlayer direction (i.e., the *c*-axis), where the structural expansion is more significant. The β angle shows a slight increase at high doping levels (reaching 99.80° at 100%), indicating minor lattice distortion. Nevertheless, no additional phases are detected in the XRD patterns, suggesting that I atoms are incorporated into the lattice in the form of a solid solution, leading to the formation of a continuous $\text{Bi}_4\text{O}_5\text{Br}_{2-x}\text{I}_x$ solid solution [20].

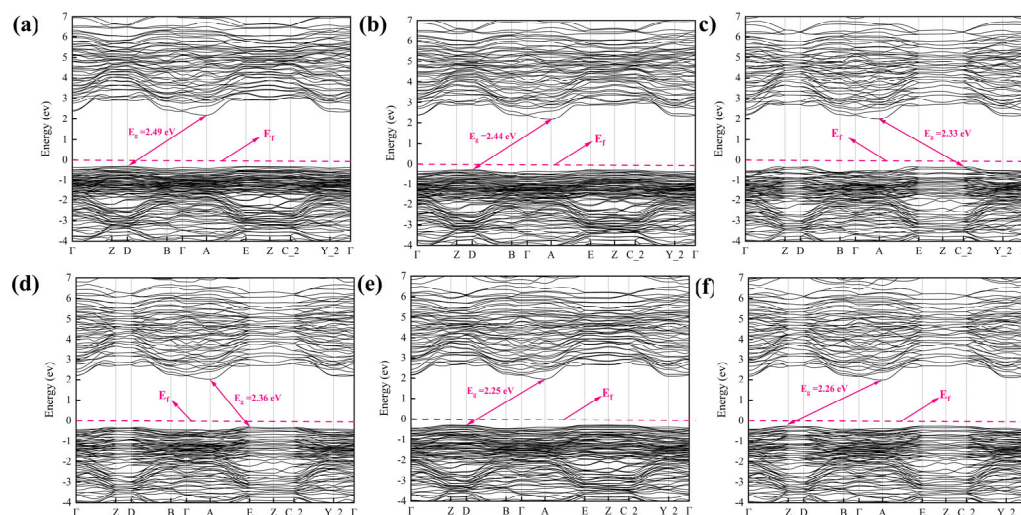


Figure 3. Energy band structure of I-doped $\text{Bi}_4\text{O}_5\text{Br}_2$ with different concentrations (a) 12.5%, (b) 25%, (c) 50%, (d) 75%, (e) 87.5%, (f) 100%.

Table 1. Optimized lattice parameters of I-doped $\text{Bi}_4\text{O}_5\text{Br}_2$ at different concentrations.

Structure	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)
$\text{Bi}_4\text{O}_5\text{Br}_2$	11.10	5.74	14.80	90.00	98.38	90.00
12.5% I- $\text{Bi}_4\text{O}_5\text{Br}_2$	11.17	5.75	14.79	89.97	98.34	89.91
25% I- $\text{Bi}_4\text{O}_5\text{Br}_2$	11.15	5.76	14.87	89.84	98.42	89.91
50% I- $\text{Bi}_4\text{O}_5\text{Br}_2$	11.20	5.78	14.95	90.00	98.53	90.00
75% I- $\text{Bi}_4\text{O}_5\text{Br}_2$	11.37	5.80	14.99	90.00	98.95	90.00
87.5% I- $\text{Bi}_4\text{O}_5\text{Br}_2$	11.42	5.81	15.18	89.93	100.05	89.94
100% I- $\text{Bi}_4\text{O}_5\text{Br}_2$	11.44	5.82	15.16	90.00	99.80	90.00

2.2. Electronic Structure

2.2.1. Band Structure

The band structures of pristine and I-doped $\text{Bi}_4\text{O}_5\text{Br}_2$ at various concentrations are presented in Figure 3. Pristine $\text{Bi}_4\text{O}_5\text{Br}_2$ is identified as an indirect band gap semiconductor, with the valence band maximum (VBM) located at a different k-point (e.g., point D) and the conduction band minimum (CBM) at point A. The calculated band gap is 2.56 eV, which agrees well with the reported experimental range of 2.18–2.75 eV [21]. The calculated band gap of pristine $\text{Bi}_4\text{O}_5\text{Br}_2$ is 2.56 eV, which falls within the experimentally reported range of 2.18–2.75 eV and is also consistent with previously reported PBE calculations (Table S1) [21]. These comparisons demonstrate that the adopted GGA-PBE approach provides a reasonable description of the electronic structure of $\text{Bi}_4\text{O}_5\text{Br}_2$. Although conventional GGA-PBE calculations may underestimate the absolute band gap of semiconductors, they have been shown to reliably capture the relative changes in electronic structure induced by elemental substitution. Therefore, the present computational approach is suitable for investigating the concentration-dependent evolution of the electronic and optical properties of $\text{Bi}_4\text{O}_5\text{Br}_{2-x}\text{I}_x$.

Upon I substitution, all systems retain their indirect band gap nature. As the doping concentration increases, the band gap generally decreases, with values of 2.49 eV (12.5%),

2.44 eV (25%), 2.33 eV (50%), 2.36 eV (75%), 2.25 eV (87.5%), and 2.26 eV (100%). The reduction in band gap is primarily attributed to the introduction of shallow impurity states near the VBM by I 5*p* orbitals, which lowers the excitation energy required for electron transition from the valence band to the conduction band [22]. A slight increase in the band gap is observed at 75% substitution (2.36 eV), which may be associated with local structural or configurational variations. Nevertheless, the overall trend remains a gradual decrease in band gap with increasing I concentration.

2.2.2. Density of States

To further elucidate the microscopic mechanism by which I doping modulates the electronic structure, the density of states (DOS) for systems with different I concentrations was calculated, as shown in Figure 4. The energy range from -5 eV to the Fermi level is defined as the upper valence band, while the range from -12 eV to -7 eV corresponds to the lower valence band.

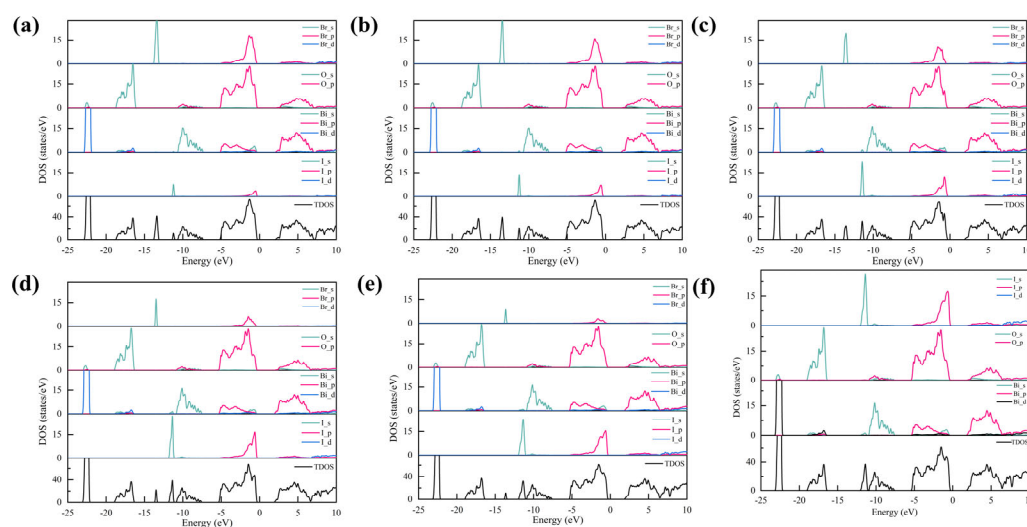


Figure 4. Density of states of I-doped $\text{Bi}_4\text{O}_5\text{Br}_2$ with different concentrations (a) 12.5%, (b) 25%, (c) 50%, (d) 75%, (e) 87.5%, (f) 100%.

For pristine $\text{Bi}_4\text{O}_5\text{Br}_2$, the upper valence band is primarily composed of Br 4*p* and O 2*p* orbitals, with a minor contribution from Bi 6*p* states. The lower valence band is dominated by Bi 6*s* orbitals, whereas the conduction band mainly consists of Bi 6*p* and O 2*p* orbitals [23].

Upon I substitution, I 5*p* orbitals progressively emerge in the upper valence band region. With increasing doping concentration, the contribution from Br 4*p* orbitals is gradually replaced by that of I 5*p* orbitals. At high doping levels (87.5% and 100%), the upper valence band becomes predominantly composed of I 5*p* and O 2*p* orbitals. In the lower valence band, Bi 6*s* states remain dominant, while the contribution of I 5*s* orbitals increases with doping concentration. In contrast, the composition of the conduction band remains largely unchanged and continues to be dominated by Bi 6*p* orbitals.

For comparison, the present results were evaluated alongside the previously reported S-substituted $\text{Bi}_4\text{O}_5\text{Br}_2$ system [19]. Similar to S doping, I substitution effectively modifies the electronic structure of $\text{Bi}_4\text{O}_5\text{Br}_2$ and results in band-gap narrowing, indicating that anion substitution is an effective approach for tuning the electronic properties of this material. However, the electronic modulation mechanisms are different. As shown by the present DOS analysis, I substitution progressively replaces the contribution of Br 4*p* states with I 5*p* states near the valence-band maximum, whereas the conduction band remains nearly unchanged. Consequently, the valence-band maximum shifts upward with

increasing I substitution, leading to a reduced band gap [24]. These results suggest that I substitution regulates the valence-band electronic structure through the introduction of I 5p states, providing a distinct electronic modulation pathway compared with the previously reported S-substituted system.

2.2.3. Differential Charge Density

The differential charge density distributions of $\text{Bi}_4\text{O}_5\text{Br}_2$ with various I substitution concentrations are presented in Figure 5 (yellow: electron accumulation; blue: electron depletion). In pristine $\text{Bi}_4\text{O}_5\text{Br}_2$, the electron density is relatively uniformly distributed around O atoms, and pronounced charge overlap is observed in the Bi-O bonding regions, indicating strong covalent interaction [25].

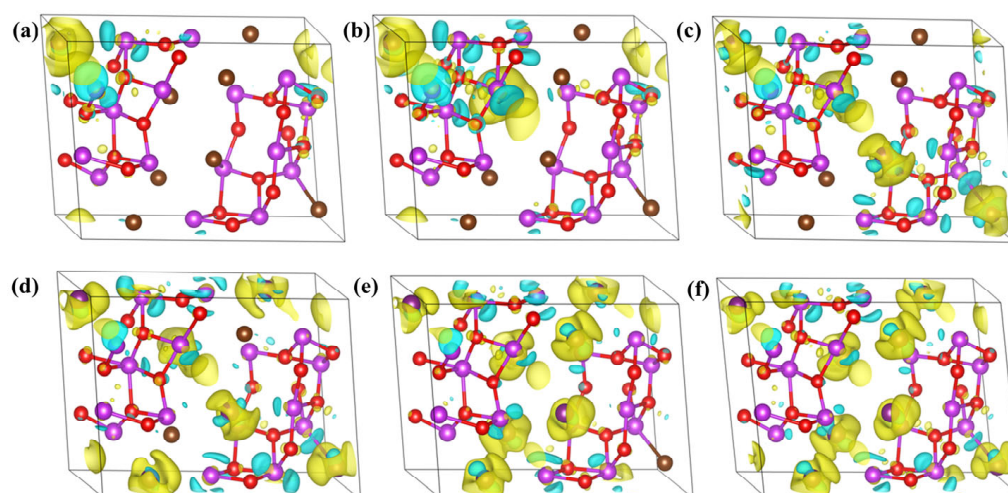


Figure 5. Differential charge density of I-doped $\text{Bi}_4\text{O}_5\text{Br}_2$ with different concentrations (a) 12.5%, (b) 25%, (c) 50%, (d) 75%, (e) 87.5%, (f) 100%.

Upon I substitution, significant electron accumulation appears around the I atoms, accompanied by electron depletion in the neighboring Bi regions. This clearly indicates charge transfer from Bi to I atoms [26]. As the I concentration increases, the extent of charge redistribution becomes more pronounced, leading to the formation of electron-rich regions centered on I atoms and electron-deficient regions around Bi atoms. Consequently, the original charge balance within the Bi-O-Br framework is progressively perturbed.

At higher doping levels (e.g., 87.5% and 100%), extended regions of electron accumulation are observed, suggesting enhanced local polarization. Such polarization effects are favorable for the separation of photogenerated electron-hole pairs, which is beneficial for photocatalytic performance [27].

To further quantify the charge redistribution induced by I substitution, Bader charge analysis was carried out, and the results are summarized in Figure 6. As the I substitution concentration increases, the Bader charges of Bi atoms become slightly less negative, indicating gradual electron depletion around Bi atoms. In contrast, the substituted I atoms carry positive Bader charges of approximately 0.58–0.61 e, whereas the charge state of O atoms remains essentially unchanged. Only minor variations are observed for the remaining Br atoms before complete substitution. These results quantitatively support the differential charge density analysis, demonstrating that charge redistribution mainly occurs between Bi and the substituted halogen atoms, thereby enhancing local polarization while preserving the overall electronic environment of the oxygen framework.

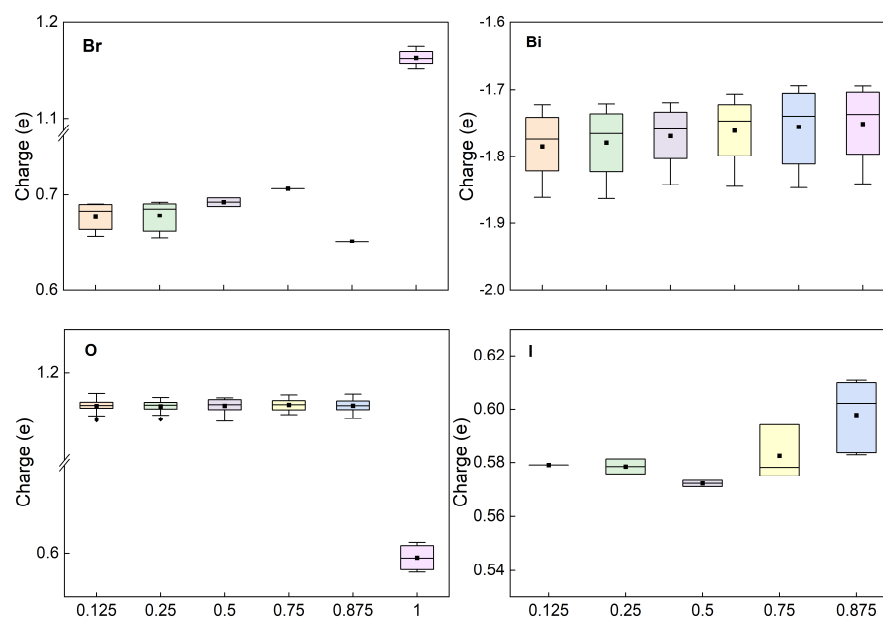


Figure 6. Statistical distributions of Bader charges for Bi, Br, O, and I atoms in $\text{Bi}_4\text{O}_5\text{Br}_2$ with different I substitution concentrations.

2.3. Optical Properties

2.3.1. Absorption Spectra

Figure 7 presents the absorption spectra of $\text{Bi}_4\text{O}_5\text{Br}_2$ with different I doping concentrations, together with an enlarged view of the low-energy region. The absorption edge of pristine $\text{Bi}_4\text{O}_5\text{Br}_2$ is located at approximately 2.5 eV (corresponding to 496 nm), and its absorption in the visible region is relatively weak.

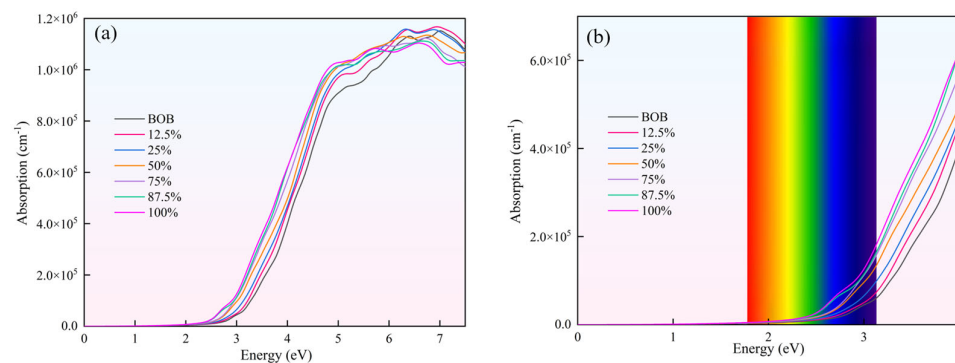


Figure 7. (a) Absorption spectra and (b) localized magnification of $\text{Bi}_4\text{O}_5\text{Br}_2$ doped with different concentrations of I.

Upon I substitution, the absorption edge gradually shifts toward lower energies (red shift), accompanied by a significant enhancement of absorption intensity in the visible-light region (1.5–3 eV). The main absorption peak in the high-energy region (around 7 eV) is attributed to electronic transitions from the upper valence band, mainly composed of O 2p, Br 4p, I 5p, and Bi 6s orbitals, to the conduction band dominated by Bi 6p and O 2p orbitals [28]. The intensity of this peak increases with increasing I concentration.

In the low-energy region (1–2 eV), additional weak absorption peaks emerge, which can be attributed to transitions from I 5p impurity states to the conduction band minimum. These results demonstrate that I doping enhances the visible-light absorption of $\text{Bi}_4\text{O}_5\text{Br}_2$ by narrowing the optical band gap and introducing impurity energy levels.

2.3.2. Dielectric Function

Figure 8 presents the real part $\text{Re}(\epsilon)$ and imaginary part $\text{Im}(\epsilon)$ of the dielectric function of $\text{Bi}_4\text{O}_5\text{Br}_2$ at different I substitution concentrations as a function of photon energy. The real part reflects the polarization response of the material, while the imaginary part corresponds to electronic transition absorption [29].

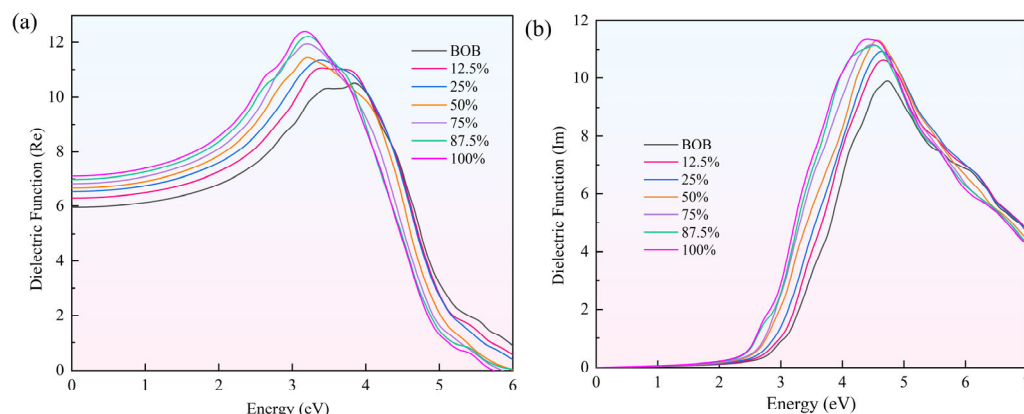


Figure 8. Dielectric function of I-doped $\text{Bi}_4\text{O}_5\text{Br}_2$ with different concentrations for the (a) real part and (b) imaginary part.

In the low-energy region (0–4 eV), the peak intensity of $\text{Re}(\epsilon)$ increases progressively with increasing I concentration and shifts toward lower energies, indicating an enhanced polarization response [30]. Correspondingly, the static dielectric constant $\epsilon_1(0)$ increases from 5.94 for pristine $\text{Bi}_4\text{O}_5\text{Br}_2$ to approximately 8.5 at 100% doping. The $\text{Im}(\epsilon)$ spectra exhibit a similar red shift and intensity enhancement. In addition, a new dielectric peak emerges at around 1–2 eV, which can be attributed to electronic transitions from I 5p impurity states to the conduction band.

In the high-energy region (>4 eV), the dielectric response is dominated by intrinsic interband transitions, and the peak intensity shows a slight increase with increasing I substitution level. The dielectric function results are consistent with the absorption spectra, further confirming that I doping effectively enhances the visible-light response of $\text{Bi}_4\text{O}_5\text{Br}_2$ [31].

2.4. CO_2 Reduction Mechanism

To evaluate the effect of I substitution on the photocatalytic CO_2 reduction performance of $\text{Bi}_4\text{O}_5\text{Br}_2$, the Gibbs free energy changes for the reduction of CO_2 to CO on the (020) surface were calculated for both pristine and I-doped systems [32]. The results are shown in Figure 9. The reaction pathway includes CO_2 adsorption to form $^*\text{CO}_2$, the first proton-electron transfer to form $^*\text{COOH}$, the second hydrogenation to form $^*\text{CO}$, and finally CO desorption [33].

For pristine $\text{Bi}_4\text{O}_5\text{Br}_2$, the Gibbs free energy for $^*\text{COOH}$ formation is 2.83 eV, which is the rate-determining step of the reaction [34]. The Gibbs free energy of the $^*\text{CO}$ intermediate is 1.28 eV, while the CO desorption step shows a relatively small energy change. After I doping, the Gibbs free energy for $^*\text{COOH}$ formation decreases to 2.68 eV, reduced by 0.15 eV. The free energy of the $^*\text{CO}$ intermediate decreases to 0.98 eV, reduced by 0.30 eV. The initial CO_2 is adsorbed, suggesting improved thermodynamic favorability of the reaction mechanistically; the I 5p states introduced by substitution modify the surface electronic structure and enhance the stabilization of $^*\text{COOH}$ and $^*\text{CO}$ intermediates, thereby facilitating the thermodynamically favorable progression of the CO_2 reduction process. Thus, I substitution effectively tailors the electronic structure and surface charge distribution

of $\text{Bi}_4\text{O}_5\text{Br}_2$, resulting in band-gap narrowing and enhanced visible-light absorption. These findings demonstrate that halogen substitution is an effective strategy for tuning the electronic structure, optical response, and reaction thermodynamics of $\text{Bi}_4\text{O}_5\text{Br}_2$, providing theoretical insights for the rational design of visible-light-responsive photocatalysts for CO_2 reduction.

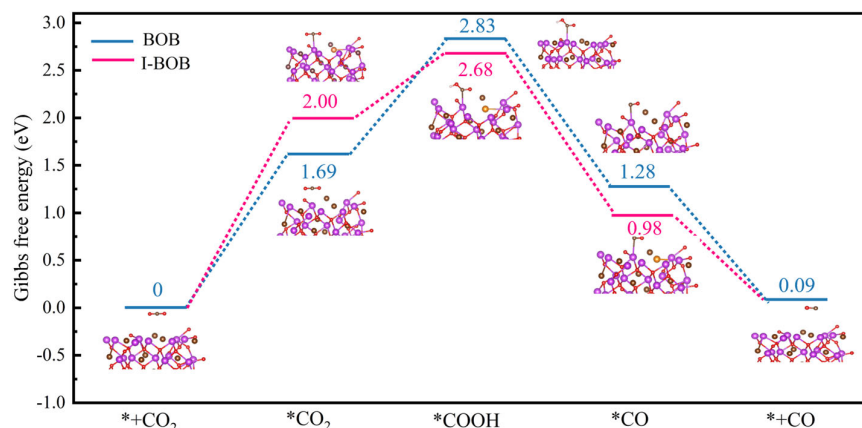


Figure 9. Paths and activation energies of intrinsic and I-doped $\text{Bi}_4\text{O}_5\text{Br}_2$ (020) in the CO_2 reduction reaction.

3. Computational Details

All calculations in this study were performed within the framework of density functional theory (DFT) using the VASP package [35]. The electron-ion interactions were described by the projector augmented wave (PAW) method. The exchange-correlation functional was treated using the generalized gradient approximation (GGA) in the Perdew–Burke–Ernzerhof (PBE) form [36,37]. The plane-wave cutoff energy was set to 500 eV. The total energy convergence criterion was 1×10^{-5} eV, and the force convergence threshold was 0.01 eV/Å. Brillouin zone sampling was carried out using a Monkhorst–Pack scheme with a k-point mesh of $3 \times 6 \times 2$. Spin polarization was included in all calculations [38].

The crystal structure of pristine $\text{Bi}_4\text{O}_5\text{Br}_2$ was obtained from the Materials Project database. To construct models with different I substitution concentrations, I atoms were introduced by randomly substituting Br atoms using the Python 3.11.4 scripting module in Materials Studio (MS). The doping concentration was defined by the number of substituted sites ($n = 1, 2, 4, 6, 7, 8$), corresponding to 12.5%, 25%, 50%, 75%, 87.5%, and 100%, respectively. For each concentration, multiple symmetry-inequivalent configurations were generated (4, 16, 38, 16, 4, and 1, respectively). All configurations were fully optimized without symmetry constraints, and the structure with the lowest total energy was selected as the representative model for each concentration (Figure 10).

To evaluate the structural stability, the formation energy of each model was calculated using first-principles methods. The formation energy (ΔE_X) was used to assess the thermodynamic stability of the doped systems and is defined as [39]:

$$\Delta E_X = E_{X\text{-BOB}} - E_{\text{BOB}} + n E_{\text{Br}} - n E_X$$

where n is the number of dopant atoms, $E_{X\text{-BOB}}$ is the total energy of the I-doped system, E_{BOB} is the total energy of pristine $\text{Bi}_4\text{O}_5\text{Br}_2$, E_{Br} is the energy of an isolated Br atom, and E_X is the energy of an isolated I atom.

Kinetic stability at finite temperature was evaluated by ab initio molecular dynamics (AIMD) simulations. For each doping concentration, the configuration with the highest for-

mation energy was selected for testing. Simulations were performed in the NVT ensemble at 300 K using a Nosé thermostat, with a time step of 1.0 fs and a total simulation time of 6 ps (6000 steps). Temperature fluctuations, total energy evolution, and structural integrity were monitored throughout the simulations.

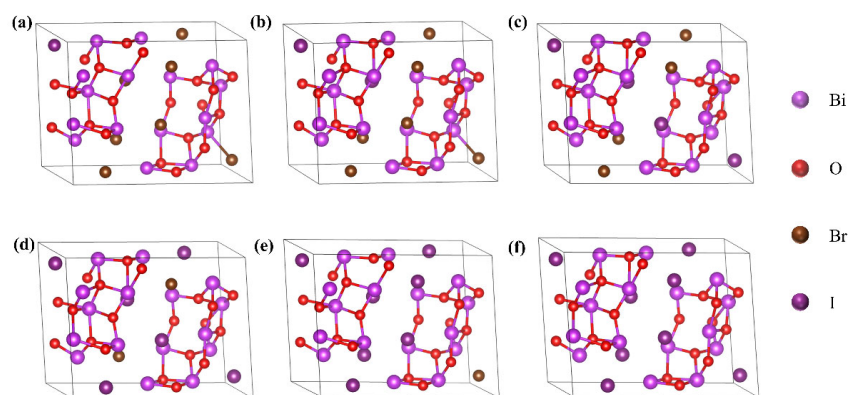


Figure 10. Structural models of I-doped $\text{Bi}_4\text{O}_5\text{Br}_2$ at (a) 12.5%, (b) 25%, (c) 50%, (d) 75%, (e) 87.5%, and (f) 100% concentration.

Based on the optimized structures, the electronic properties were analyzed through band structure and density of states (DOS) calculations. Band structures were plotted along high-symmetry paths in the Brillouin zone, and DOS calculations employed the same k-point mesh. Post-processing was conducted using VASPKIT 1.5.1 [40], and structural and electronic visualizations were generated with VESTA 6.5.1 [41]. The differential charge density was obtained by subtracting the superposition of isolated atomic charge densities from the self-consistent charge density, in order to analyze charge redistribution induced by I doping.

Optical properties were evaluated from the frequency-dependent dielectric function, $\epsilon(\omega) = \epsilon_1(\omega) + i \epsilon_2(\omega)$, where $\epsilon_1(\omega)$ represents the polarization response and $\epsilon_2(\omega)$ corresponds to electronic transition absorption. The absorption coefficient $\alpha(\omega)$ was derived from the dielectric function. The calculations were performed with `LOPTICS = .TRUE.` under the independent particle approximation.

Surface models were constructed by cleaving the optimized bulk structure along the (020) plane. The slab thickness was approximately 21.8 Å, and a vacuum layer of 15 Å was introduced along the surface normal to eliminate interactions between periodic images. The bottom two atomic layers were fixed to mimic the bulk environment, while the remaining atoms and adsorbates were fully relaxed. The Gibbs free energy changes (ΔG) of each elementary step in the CO_2 reduction pathway were calculated using the computational hydrogen electrode (CHE) model [42]. The reaction intermediates considered include $^*\text{CO}_2$, $^*\text{COOH}$, $^*\text{CO}$, and CO desorption. The adsorption free energies were obtained from total energy differences with zero-point energy and entropy corrections.

4. Conclusions

In this work, first-principles density functional theory (DFT) calculations were employed to systematically investigate the effects of I substitution at different concentrations (12.5%, 25%, 50%, 75%, 87.5%, and 100%) on the geometric structure, electronic structure, optical properties, and photocatalytic CO_2 reduction performance of $\text{Bi}_4\text{O}_5\text{Br}_2$. The main conclusions are as follows:

- (1) The I^- substituted systems exhibit good thermodynamic and kinetic stability. The formation energy increases with doping concentration (from 0.558 eV to 4.87 eV), while AIMD simulations show that all substituted systems remain structurally intact

at 300 K, with no bond breaking or structural collapse. I substitution leads to an overall expansion of lattice parameters, especially along the c-axis (from 14.80 Å to 15.16 Å), due to the larger ionic radius of I^- compared to Br^- . The system maintains a single-phase solid solution structure.

- (2) After I substitution, $Bi_4O_5Br_2$ remains an indirect band gap semiconductor, with the band gap decreasing from 2.56 eV in the pristine system to 2.25 eV at 87.5% substitution. Density of states analysis shows that I 5p orbitals progressively replace Br 4p orbitals as the main contributors to the upper valence band, thereby tuning the valence band maximum and reducing the band gap. Differential charge density results indicate electron transfer from Bi atoms to I atoms, forming electron-rich regions centered on I and enhancing local polarization, which is beneficial for photogenerated carrier separation.
- (3) Optical property calculations indicate a pronounced red shift in the absorption edge after I substitution, along with a significant enhancement of absorption intensity in the visible region (1.5–3 eV). New absorption peaks appear in the low-energy region due to I 5p impurity states. Both the real and imaginary parts of the dielectric function exhibit red shifts and increased peak intensities in the low-energy region. The static dielectric constant also increases, indicating improved polarization response and light absorption capability.
- (4) Gibbs free energy analysis shows that I substitution effectively reduces the Gibbs free energy of the rate-determining step (*COOH formation) in CO_2 reduction, from 2.83 eV to 2.68 eV. The free energy of the *CO intermediate is also reduced from 1.28 eV to 0.98 eV. By introducing I 5p impurity states, I substitution regulates the surface electronic structure and enhances the stabilization of key intermediates (*COOH and *CO), thereby optimizing the reaction pathway and promoting CO formation and desorption.

In summary, I substitution is an effective strategy to regulating the electronic structure and optical properties of $Bi_4O_5Br_2$, enhancing visible-light absorption, and improving the thermodynamic characteristics of the CO_2 reduction reaction. This study provides theoretical guidance for halogen substitution as a promising approach for designing visible-light-responsive photocatalysts.

Supplementary Materials: The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/catal16070622/s1>, Table S1: Comparison of Experimental and Theoretical Band Gaps of $Bi_4O_5Br_2$ [14,21,22,32,33,43–47].

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