



Article Synergistic Effects of B-F/B-S and Nitrogen Vacancy Co-Doping on g-C₃N₄ and Photocatalytic CO₂ Reduction Mechanisms: A DFT Study

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Abstract: Nonmetallic co-doping and surface hole construction are simple and efficient strategies for improving the photocatalytic activity and regulating the electronic structure of g-C₃N₄. Here, the g-C₃N₄ catalysts with B-F or B-S co-doping combined with nitrogen vacancies (N_v) are designed. Compared to the pristine g-C₃N₄, the direction of the excited electron orbit for the B-F-co-doped system is more matching (N_{2pz} \rightarrow C_{2pz}), facilitating the separation of electrons and holes. Simultaneously, the introduced nitrogen vacancy can further reduce the bandgap by generating impurity states, thus improving the utilization rate of visible light. The doped S atoms can also narrow the bandgap of the B-S-N_v-co-doped g-C₃N₄, which originates from the p-orbital hybridization between C, N, and S atoms, and the impurity states are generated by the introduction of N vacancies. The doping of B-F-N_v and B-S-N_v exhibits a better CO₂ reduction activity with a reduced barrier for the rate-determining step of around 0.2 eV compared to g-C₃N₄. By changing F to S, the origin of the rate-determining step varies from *CO₂ \rightarrow *COOH to *HCHO \rightarrow *OCH₃, which eventually leads to different products of CH₃OH and CH₄, respectively.

Keywords: g-C₃N₄ nonmetallic element co-doping; nitrogen vacancies; electronic structure modification; photocatalytic CO₂ reduction mechanism

1. Introduction

Fossil fuels are a vital source of energy for human beings [1]; however, the use of fossil fuels releases CO_2 to accumulate in the atmosphere, leading to a serious greenhouse effect [2,3]. Finding efficient ways to reduce CO₂ emissions or capture CO₂ and convert it into chemical commodities is the key problem to solve [4-7]. Lightweight materials with different nano-morphologies containing heteroatoms have been actively pursued for catalytic applications and as semiconductor materials because of their unusual properties [8]. Graphitic carbon nitride $(g-C_3N_4)$ is a star two-dimensional metal-free semiconductor material with a bandgap of 2.7 eV [9]. Unfortunately, the catalytic reduction of CO₂ using pristing $g-C_3N_4$ is very inefficient due to the fast recombination of photogenerated holes and electrons and the low utilization efficiency of visible light [10,11]. To improve the photocatalytic efficiency of pristine g-C₃N₄, many studies have been carried out, including structure optimization, doping modification [12–15], structural and defect engineering [16], and composite heterojunction materials [17–23]. Experimental studies have shown that nonmetallic doping, such as B, O, S, P, and halogen doping, is an effective way to enhance the photocatalytic performance and maintains the metal-free photocatalytic properties of $g-C_3N_4$ [24–27]. Yan found that boron-doped $g-C_3N_4$ effectively utilized visible light, increasing the photocatalytic degradation rate of rhodamine B by 3.6 times [8], while Ohno et al. applied it in the photocatalytic CO₂ reduction process and generated methanol [24]. In the halogen-doped system, the F-doped $g-C_3N_4$ was reported to have the smallest bandgap energy and the strongest light absorption ability, and the doped g-C₃N₄ was corrugated to



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enhance the structural stability, but the adsorption energy of CO_2 was small, which was not conducive to the subsequent restoration process [22]. Liu, and Wang et al. [6,28] reported the S-doped g-C₃N₄ material; the bandgap was significantly reduced, the adsorption of CO_2 was enhanced, and it was reduced to methanol, but the reason for the separation of electrons and holes was not explained.

Recently, researchers have focused on the double-element doped system. The characteristics of continuous tuning can be exhibited by changes in the composition of host and guest elements and flexible modification of the electronic structure and/or geometry of the two-element catalysts during synthesis, which greatly improves the ability to enhance the catalytic activity, selectivity, and stability and reduce catalyst cost [29,30]. Cui. et al. studied the B-F system, proving that the potential of the conduction band was sufficient to reduce CO_2 , but the expansion of the bandgap limited the further development in the field of photocatalysis application [25]. Han et al. studied the B-S system and demonstrated the important synergistic effect of nonmetallic co-doping on the photocatalytic reduction of CO_2 by increasing the utilization of visible light [26]. Tay, and Tu et al. proved that the introduction of the nitrogen vacancy (N_v) further improved the performance of metal-codoped materials [27,31]. Wang et al. further revealed in the B-K-N_v experiment that N_v can enrich electrons and was more prone to chemical reactions [32]. However, metals tend to form TM-H bonds with hydrogen during catalysis, leading to a low Faraday efficiency. In addition, metal ions tend to spill over and cause environmental pollution [33,34]. The focus of research has shifted to catalysts doped with nonmetallic elements, which, to some extent, eliminates the environmental problems of metallic catalysts [35]. Defect engineering is another effective strategy to modulate catalyst performance, which improves catalytic performance by introducing impurity states to reduce the bandgap [36]. In order to investigate how vacancies interact with nonmetallic elements to improve catalytic performance, this paper designs the nonpolluting and efficient catalysts using double nonmetallic elements coupled with a nitrogen vacancy to investigate the microscopic reaction mechanism of carbon dioxide reduction.

First-principles calculations within the Density Functional Theory (DFT) method have contributed to the understanding of modifications at the atomic scale [37]. Considering the advantages of B, F, and S dopants of the narrower bandgap, stronger photocurrent response [8], sufficient utilization of visible light [22], and promotion of the separation of photogenerated carriers [38,39], in this work, the nonmetal dual elements catalysts, e.g., the B-F-N_v-co-doped g-C₃N₄ (abbreviated as B-F-N_v) catalyst, as well as the B-S-N_v-co-doped g-C₃N₄ (abbreviated as B-S-N_v), were designed. The nitrogen vacancy was also introduced here, as it could introduce additional energy levels and/or act as reaction sites [40,41]. Importantly, the possible reaction pathways for CO₂ reduction to C1 products were further investigated. It is of interest to investigate how the nonmetallic co-doping combined with nitrogen vacancies synergistically modulates the photocatalytic performance and facilitates reduction of CO₂. By calculating the Gibbs free energy change (Δ G) and the product adsorption energy, the species of CO₂ final reduction products were determined.

2. Computational Methods

The electronic structural properties of the pristine and doped g-C₃N₄ catalysts were calculated using the Vienna Ab-initio Simulation Package (VASP) [42], and the projected plus plane wave (PAW) pseudopotential [40] was used to describe the interaction between ionic real and valence electrons. The unit cell energy and lattice constant were calculated using the PBE functional of the generalized gradient approximation method (GGA) [43]. During the structural optimization calculations, a very precise accuracy of 1.0×10^{-6} eV was used as the criterion for energy convergence. For the K-point setting of the system, the Mokhorst–Pack setting of $3 \times 3 \times 1$ was used in the structural relaxation, and the K-point setting of $6 \times 6 \times 1$ was used in the static calculation and performance calculation. Considering that the PBE method tended to underestimate the bandgap value, the band structures of the pristine and doped systems were calculated using the HSE06 hybrid

functional [44,45]. In order to avoid mutual interference between adjacent systems, a vacuum space of 15 Å was introduced and the energy cutoff value of the system was set to 450 eV, and the effect of spin polarization was considered in the calculation. The PBE (D3) method with the Grimme van der Waals correction was employed because of the weak interactions between CO_2 Photocatalytic Reduction (CO_2RR) Reaction species and catalysts [46].

Pure bulk g-C₃N₄ is built on the hexagonal heptadiazine-based structure as it is the most stable graphitic phase [47], and it contains two or three different kinds of C and N atoms, which are marked as C1-C2 and N1-N3, respectively, as shown in Figure 1a,b. According to the experimental results, B-N bonds and N-F bonds existed in the XPS spectra of B-F-co-doped g-C₃N₄ [25], indicating that B atoms preferentially replaced C atoms (C1), and F atoms tended to combine with N atoms (N2) to be doped into the interspace, as shown in Figure 1c. There are 5 possible sites where N_v can be introduced, namely, N_v1-N_v5 in B-F-co-doped g-C₃N₄, as shown in Figure 1c. For B-S-co-doped g-C₃N₄, similar possible doping sites are provided, as given in Figure 1d, based on the experiment [26]. The optimal doping site can be determined by the formation energy (E_{form}), according to the following equation:



Figure 1. Pristine and doped $g-C_3N_4$ geometries. (a) Top view of pristine $g-C_3N_4$ geometry. (b) Side view of pristine $g-C_3N_4$ geometry. (c) N_v sites of B-F-N_v. (d) N_v sites of B-S-N_v.

 $E_{undoped}$ and E_{doped} are the electron energies of the catalysts before and after doping, respectively. μA and μB are the chemical potentials of the substituted atoms, i.e., μC , μN , μB , μF , and μS . Formation energy can also reflect the difficulty of doping; the lower the formation energy, the better the thermodynamic stability.

3. Results and Discussion

3.1. Geometric Structure and Thermodynamic Stability

The formation energy results are shown in Table S1 to determine the location of nitrogen vacancies. The E_{form} of the doped N_v4 site of B-F-N_v is lowest among the possible doping sites, indicating that it is the most stable structure, and the negative value of -0.55 eV suggests that the introduction of N_v is thermodynamically spontaneous [41] and easier to synthesize experimentally. In contrast, the lowest E_{form} of B-S-N_v is 1.07 eV, corresponding to the doped site of N_v2 , suggesting that it is more difficult to introduce N_v on the basis of B-S than B-F-doped g-C₃N₄.

To explain how the doped elements and vacancies affect the properties of pristine $g-C_3N_4$, the optimized bond length parameters for pure $g-C_3N_4$, B-F, and B-F-N_v-doped $g-C_3N_4$ are shown in Figure 2, Table S2 and compared with the experimental [48] and theoretical values [28]. It can be seen that the optimized geometric parameters agree well with the available results; the maximum deviations from theory and experiment are 0.02 and 0.13 Å, respectively, verifying the reliability of the calculation method and parameter settings. Figure 2a–d show the variation in the key bond lengths from g-C₃N₄, B-F, and B-F-N_v to B-S-N_v. Compared to the pristine $g-C_3N_4$, the introduction of elements and holes only changes the local geometry of the doping site and has little effect on other sites for the doped g- C_3N_4 . The dramatic change lies in B (C2)-N1 bonds, which is elongated from 1.47 and 1.51 to 1.62 Å gradually from $g-C_3N_4$ to the introduction of B and F atoms and then the nitrogen vacancies. This is because the radius of the B atom (0.88) is larger than that of the C atom (0.77) and the electronegativity of the F atom (3.98) is stronger. For B-F-co-doped $g-C_3N_4$, the introduction of the F atom with the stronger electronegativity can facilitate the electrons flowing to the F atom, thus weakening the B-N bond. With the further introduction of N_v , the F atom shifts from N2 to the B atom, and importantly, the C atom changes from sp² hybridization to sp hybridization, leading to the enhanced electronegativity of the C atom. Thus, the interaction between the C and the N atom is further enhanced, and the interaction between the N and the B atom is weakened, leading to the further elongation of the B-N bond. Similarly, for $B-S-N_v$, the introduction of B and S elements and N_v extends the distance of the B-N1 bond to 1.53 A. Due to the absence of N, the structure changes from a six-membered ring to a five-membered ring at the nitrogen vacancy ring, and local large deformation occurs. Generally, with the degree of local deformation of the geometric structure increased, the mutual repulsion between the lone pairs of electrons of the N atom in the system will reduce and the material will become more stable [49].



Figure 2. The optimized geometries and bond lengths of $g-C_3N_4$ (a), B-F (b), B-F-N_v (c), and B-S-N_v (d).

3.2. Electronic Structure and Electronic Properties

The bandgaps of g-C₃N₄, and B-F-, B-F-N_v-, and B-S-N_v-co-doped g-C₃N₄ calculated by different methods are listed in Table S3 together with experimental and literature values [8,14,25]. The bandgap values calculated by the HSE06 hybrid functional in this paper are in good agreement with those of previous studies [24,50], again testifying the rationality of the structures. Due to the limitations of the GGA method, the multi-electron interactions cannot be fully described, and the bandgap value is often underestimated, but it does not affect the results of qualitative comparisons and the rules. The results show that B-F co-doping increases the bandgap value from 2.77 to 3.06 eV compared to g-C₃N₄, while the injection of N_v significantly reduces the bandgap value from 3.06 to 2.67 eV, which facilitates the broadening of the visible light utilization.

The band structure and contribution of atoms and atomic orbitals to the density of states for g-C₃N₄, and B-F-N_v- and B-S-N_v-co-doped g-C₃N₄ are presented in Figure 3. It can be seen that the valence band maximum (VBM) and conduction band minimum (CBM) for g-C₃N₄ are located at point Gamma and point K, respectively. Due to the different positions of the VBM and CBM in k-space, g-C₃N₄ is an indirect bandgap semiconductor with a bandgap value of 2.77 eV calculated by the HSE06 method. The valence band is mainly contributed by N_(2px, 2py) orbitals of N atoms, while the conduction band is mainly C_{2pz} of C atoms and a small amount of N_{2pz} orbitals of N atoms. Due to the different orbital orientations, it is difficult to excite electrons from N_(2px, 2py) to C_{2pz} or N_{2pz} orbitals, which is one of the reasons for the difficult transition of photogenerated electrons and low carrier mobility in g-C₃N₄ [51].



Figure 3. Calculated band structure (**left**), density of states (**middle**), and partial density of states (**right**) diagrams of $g-C_3N_4$ (**a**), B-F-N_v (**b**), and B-S-N_v (**c**).

In contrast, B-F-N_v is a direct bandgap structure with a value of 2.67 eV calculated by the HSE06 method, smaller than $g-C_3N_4$, as both VBM and CBM are located at point Gamma. The direct transition of electrons reduces the energy loss caused by electron relaxation, which means a higher energy conversion efficiency [52–54]. The loss of nitrogen atoms caused by vacancies destroys the π -conjugation of g-C₃N₄, leading to the reconstruction of the band structure and the formation of impurity states in the middle of the forbidden band. Due to the low doping concentration of B (1.73 at.%) and F (1.75 at.%) atoms, the contribution of both types of atoms to the band edges is not obvious [49]. The introduction of nitrogen vacancies generates additional electron and spin polarization in $g-C_3N_4$, and an impurity state is created in the middle of the forbidden band of the spin states. The valence band consists mainly of N_{2pz} and N_(2px, 2py) orbitals and the conductive band is mainly composed of C_{2pz} orbitals. As the electron transition orbital direction is the same, it is easier to realize the electron transition and improve the carrier mobility. The impurity state consists of C_{2pz} and N_{2pz} orbitals, which belong to the hanging bonds of carbon atoms in nitrogen vacancies [27]. The composition of the impurity state is consistent with the composition at the bottom of the conduction band, which can receive the electrons excited at the top of the valence band and shift the light absorption wavelength to the long-wave direction. This facilitates continuous photoexcitation of the VBM to CBM in the visible light range.

Compared to $g-C_3N_4$ and $B-F-N_v$, $B-S-N_v$ is also a direct bandgap structure and the doped S atoms can further narrow the bandgap, as shown in Table S3. The PBE method is used to calculate the bandgap values for $g-C_3N_4$, $B-F-N_v$, and $B-S-N_v$ as 1.21, 1.19, and 1.16 eV, respectively. By contrast, the impurity level is generated at near the VBM due to the introduction of nitrogen vacancies, which is mainly contributed by the N_{2pz} orbital. As shown in Figure 3c, the VBM is contributed by N atoms and a small amount of C and S atoms. The overlap of electronic states of S and C indicates the hybridization of S and C atomic orbitals, while the CBM is mainly contributed by C atoms and a small amount of N atoms. The B atoms have little contribution to the energy band edges and do not directly participate in the generation, separation, and migration of photogenerated carriers, but act as electron donors to enhance the photocatalytic performance of $g-C_3N_4$ by affecting the charge distribution of surrounding atoms [8]. The formed impurity state at the top of the valence band of the spin-down state consists of hybridized C_{2pz} , N_{2pz} , and S_{3pz} orbitals. This is because the doped S atoms affect the distribution of C and N atoms in the lattice, resulting in p-orbital hybridization between C, N, and S atoms.

Figure 4 presents the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of g-C₃N₄, B-F-N_v, and B-S-N_v. For g-C₃N₄, the HOMO covers all the corner N atoms, while the LUMO is mainly distributed on the C and N atoms. The bridge N atoms are not involved in either the valence or the conduction band, so they do not excite or accept electrons, hindering the transfer of charge carriers between the heptylhydrazine rings by bridging N atoms. Both photogenerated electrons and holes are concentrated on each heptylhydrazine ring, resulting in a high carrier recombination rate and poor photocatalytic activity due to the spatial overlap of HOMO and LUMO orbitals. In contrast, the charge density rearranges and electron-rich regions appear for both B-F-N_v and B-S-N_v. The HOMO orbitals are mainly distributed on the N_v-introduced building blocks, while the LUMO orbitals are mainly on the remaining unmodified heptyltriazine rings, which differs from the spatial overlap of the HOMO and LUMO orbitals of $g-C_3N_4$, as shown in Figure 4b,c. The HOMO and LUMO orbitals of B-F-N_v and B-S-N_v are completely spatially separated, which will effectively improve the separation efficiency of photogenerated electrons and holes. In addition, the HOMO and LUMO orbitals are also distributed on the bridged N atoms, which facilitates the carrier migration between the heptatriazine ring building blocks and increases the carrier mobility [55,56].



Figure 4. HOMO and LUMO for $g-C_3N_4$ (a), B-F-N_v (b), and B-S-N_v (c).

3.3. Adsorption Properties of CO₂

The effects of modification methods on the electronic and optical properties of g-C₃N₄ have been focused on extensively; however, the theoretical studies of their applications on specific photocatalytic reactions are still limited. In this work, the effects of B-F-N_v and B-S-N_v modification on the photocatalytic CO₂ reduction of g-C₃N₄ are investigated. The first step of the photocatalytic reaction is the adsorption of CO₂. Figure S1 presents the possible adsorption sites for CO₂ on B-F-N_v and B-S-N_v, together with adsorption energy, to determine the optimal adsorption site. The adsorption energy of CO₂ placed above the nitrogen vacancy in parallel (Figure S1a,b) and vertically (Figure S1c) is -0.16 eV, while that placed above the interstitial in parallel (Figure S1d) is -0.26 eV, indicating that the optimal adsorption site is above the interstitial. This may be because after modification and under the visible light excitation, holes appear around the nitrogen vacancies to generate oxidation sites and exhibit oxidation activity, while the charge density increases from -1.12 e to -1.39 e on the corner N atoms around the interstitial, as shown in Figure S3 (red cycle). Therefore, the optimal adsorption site of CO₂ on B-F-N_v is not the nitrogen vacancy with strong oxidation activity, but the interstitial with strong reduction activity.

For B-S-N_v, the adsorption energy is -1.99, -2.68, and -1.97 eV for CO₂ adsorbed above the nitrogen vacancies, above the interstitial, and on top of B and S atoms, respectively, as shown in Figure S1e–g. Thus, the optimal adsorption site of CO_2 on B-S-N_v is also above the interstitial, which is similar to B-F-N_v, but the adsorption of CO_2 on B-S-N_v is stronger than on B-F-N_v. This can be explained by the charge transfer determined by the differential charge density (CDD) map. Figure 5 is a CDD plot of CO₂ adsorption on $g-C_3N_4$, B-F-N_v, and B-S-N_v. The yellow and blue color represents electron enrichment and depletion, respectively, so charge flows from the blue area to the yellow area. In the $g-C_3N_4$ adsorption system, there are less charge distributions on the interstitial edge corner N atoms and bridging N atoms. In the B-F- N_v adsorption system, the charge transfers from the B atom to the adjacent N atom active site, and the charge around the nitrogen vacancy flows to the adsorption active site, forming a charge-rich environment at the edge N atom site. F atoms serve as bridges to transfer electrons to CO₂. However, the charge density on the bridging F atom is too high, and the electron repulsion between the bridging F and the O atom of CO_2 becomes larger, weakening the adsorption effect. In contrast, for the B-S-N_v adsorption system, the charge concentration flows to the adsorption active site, and the charge density enrichment degree on the corner N atoms at the gap edge increases, thereby enhancing the adsorption of CO₂.



Figure 5. The map of differential charge density for $g-C_3N_4$ (**a**), B-F-N_v (**b**), and B-S-N_v (**c**).

3.4. Catalytic Performance for the Photocatalytic CO₂ Reduction

Carbon dioxide is a very stable linear molecule, and the photocatalysts with a suitable conduction band potential to convert carbon dioxide into hydrocarbon fuel are highly desirable. The selectivity of g-C₃N₄ to the reduction product is still controversial and the yield is low. In addition, how the doping modification affects the catalytic performance and product selectivity of g-C₃N₄ should also be investigated. The Gibbs free energy curve and adsorption energies of products in different stages for $g-C_3N_4$, B-F-N_v, and B-S-N_v are presented in Figure 6, as well as the representative geometries of the stable points in the specific reduction process of CO_2 on g- C_3N_4 . The photocatalytic CO_2 reduction pathways are similar for all three $catalysts, i.e., *CO_2 \rightarrow *COOH \rightarrow *CO \rightarrow *CHO \rightarrow *HCHO \rightarrow *OCH_3 \rightarrow *CH_3OH \rightarrow *CH_3 \rightarrow *CH_4 \rightarrow *CH_3 \rightarrow *CH_3$ as proposed by Azofra et al. [49]. The speculated probable products are CO, HCHO, CH₃OH, and CH₄, which are 2, 4, 6, and 8 electron processes, respectively. Further, Yu et al. [57]. Experimentally synthesized a $g-C_3N_4$ catalyst and applied it to the reduction of CO_2 under UV-Vis radiation, confirming that the main product of CO₂ reduction was CH₃OH and that it reached a yield of 0.81 μ mol \cdot g⁻¹. In the Gibbs free energy diagram calculated in this paper, it can be seen that $\triangle G = -0.48$ eV when CO₂ is reduced to CH₃OH, and 0.53 eV of energy needs to be absorbed in the subsequent reaction. Therefore, it can be seen that methanol exists stably, and methanol is the final reduction product, which is consistent with the experiment [57].



Figure 6. (a) Gibbs free energy diagrams of photocatalytic CO_2 reduction and (b) adsorption ene-gies of products in different stages of CO_2 reduction for pristine and doped systems. (c) The repr-sentative geometries of the stable points in the specific reduction process for CO_2 on g-C₃N₄.

For B-F-N_v, the formation of free radicals is endothermic because breaking carbonoxygen single or double bonds requires external input energy, i.e., $*CO_2 \rightarrow *COOH$ (1), *CO \rightarrow *CHO (3), and *CH₃OH \rightarrow *CH₃ (7), which is similar to g-C₃N₄. However, the *HCHO \rightarrow *OCH₃ (5) process for B-F-N_v releases 0.46 eV of energy, which is contrary to $g-C_3N_4$. As shown in Figure S3 (blue cycle), the charge on the adsorption site of the C atom for B-F-N_v is +1.60, which is larger than those of $g-C_3N_4$ and B-S-N_v with the values of +1.45 and +1.49, respectively. The increased charge density facilitates the formation of OCH_3 to become an exothermic process, and thus is conducive to the subsequent reactions. The first hydrogenation process for B-F-N_v is the decisive step of the whole reduction reaction with the barrier of 1.05 eV, which is lower than that of $g-C_3N_4$ (1.28 eV), as shown in Figure 6a, facilitating the formation of COOH free radicals. In addition, the reaction releases energy ($\Delta G < 0$) when a neutral product is formed, such as * COOH \rightarrow *CO (2), *CHO \rightarrow *HCHO (4), *·OCH₃ \rightarrow *CH₃OH (6), *·CH₃ \rightarrow *CH₄ (8), and there is no chemical bond with the substrate in product of stage. However, the formed radicals such as COOH, ·CHO, ·OCH₃, and ·CH₃ can be bonded with the catalyst, and the adsorption sites are obviously different. For the species of C-terminal free radicals, they are easier to bond with the negatively charged N atom, and the species of O-terminated radicals are more likely to form chemical bonds with C atoms in the substrate, as shown in Figure 6c, which affects the elementary process of the reduction reaction to some extent. The energy of 0.55 eV is released when $\cdot \text{OCH}_3$ transforms to CH₃OH 6, and the adsorption energy is also favorable for desorption of methanol with the value of 0.82 eV, as shown in Figure 6b, so the final product is also CH₃OH, which is similar to g-C₃N₄ and consistent with the previous experimental results [57].

Unlike B-F-N_v, in the process of CO₂ reduction on B-S-N_v, there are two consecutive energy absorption processes (1) and (2). The reaction barrier of the first hydrogenation with the value of 0.22 eV is much lower than those of both g-C₃N₄ and B-F-N_v, which is favorable for the initial reaction. The reduction of HCHO to CH₃O (5) is the rate-determining step by the absorption energy of 1.03 eV, lower than that of g-C₃N₄. Once crossing the reaction rate-determining step, it undergoes three exothermic processes until reduction to the final product CH₄ with the small adsorption energy.

4. Conclusions

In this paper, the photocatalytic performance and photocatalytic CO₂ reduction of the nonmetallic co-doping combined with nitrogen vacancy systems, B-F-N_v and B-S-N_v, are investigated and compared to g-C₃N₄ to explore the doping effects. It is found that B-F-N_v and B-S-N_v can combine the advantages of the three modification methods to exert a synergistic effect. B-doping can compensate for the defect of the conduction band drop caused by F-doping and N_v, and maintain the high reduction potential of CO₂. With the doped F, B-F-N_v has a corrugated configuration, which reduces the repulsion between the lone pair electrons of the N atom, and improves the stability of the g-C₃N₄ structure. At the same time, F can act as a bridge for the transfer of charges from the doping system to CO₂. N_v and B atoms form a charge-rich environment at the reactive site, which makes up for the charge loss caused by F doping and S doping.

The B-F-N_v- and B-S-N_v-co-doped g-C₃N₄ have a direct bandgap structure compared to the indirect one for g-C₃N₄. The introduction of heteroatoms and nitrogen vacancies affects the charge distribution and improves the separation of the HOMO and LUMO, thereby enhancing the separation efficiency of photogenerated electrons and holes. The synergistic effect of B-S-N_v makes the charge flow to the adsorption active site, which increases the charge enrichment of corner N atoms at the gap edge in g-C₃N₄, resulting in enhanced CO₂ adsorption. B-F-N_v- and B-S-N_v-co-doped g-C₃N₄ have a lower rate-determining step than g-C₃N₄ for the rate-determining step photocatalytic CO₂ reduction. B-S-N_v has the strongest adsorption capacity for CO₂, and the desorption capacity of the reduction products is stronger than that of g-C₃N₄, but weaker than that of B-F-N_v. The suggested main reduction product is CH₃OH for CO₂ reduction catalyzed by g-C₃N₄ and B-F-N_v, and is CH_4 catalyzed by B-S-N_v. Therefore, the nonmetallic co-doping combined with N_v in this work provides a new idea for improving the catalytic performance of photocatalysts.

Supplementary Materials: The following supporting information can be downloaded at: https: //www.mdpi.com/article/10.3390/molecules27217611/s1, Figure S1: The possible adsorption sites for CO₂ on B-F-N_v (a–d) and B-S-N_v (e–g), and corresponding adsorption energy (eV); Figure S2: The reaction pathways for B-F-N_v (a) and B-S-N_v (b); Figure S3: The bader charge (unit e) of g-C₃N₄ (left), B-F-N_v (middle), and B-S-N_v (right). Negative and positive values mean gaining and losing electrons. The elements are colored in pink for B, gray for C, blue for N, red for O, cyan for F, and yellow for S; Figure S4: Calculated band structure (left), density of states (middle), and partial density of states (right) diagrams of g-C₃N₄ (a), B-F-N_v (b) and B-S-N_v (c), the energy range is from -10 eVto 10 eV; Table S1: Formation energy (eV) of B-F-N_v and B-S-N_v co-doped g-C₃N₄; Table S2: The bond length parameters of intrinsic and doped g-C₃N₄ [28,48]; Table S3: The band gap energy (eV) for the intrinsic and doped g-C₃N₄ [28,31,50].

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