Charge Modulation at Atomic-Level through Substitutional Sulfur Doping into Atomically Thin Bi$_2$WO$_6$ toward Promoting Photocatalytic CO$_2$ Reduction

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Photocatalytic reduction of CO$_2$ has attracted enormous interest as a sustainable and renewable source of energy. In the past decade, numerous bulk-type semiconductors have been developed, but the existing designs suffer many limitations, namely rapid recombination of charge carriers and weak light absorption ability. Herein, a bottom-up approach was developed to design atomically thin sulfur-doped Bi$_2$WO$_6$ perovskite nanosheets (S-BWO) with improved reduction ability, extended visible light absorption, prolonged lifetime of charge carriers, enhanced adsorption of CO$_2$, and reduced work function. Compared with pristine Bi$_2$WO$_6$ (P-BWO), S-BWO nanosheets exhibited a 3-fold improvement in photocatalytic reduction of CO$_2$ under simulated sunlight irradiation. Experimental studies and density functional theory calculations revealed the synergistic roles of atomically thin nanosheets and S atoms in promoting photocatalytic efficiency.

Introduction

With the expeditious development of industrialization, global energy demands are ever-growing. The world’s heavy reliance on non-renewable resources is worrying as they are finite, and the combustion of fossil fuels is currently the largest source of greenhouse gas emissions. Hence, aggravation of global environmental problems is inevitable. Photocatalysis comes into play as an auspicious approach for the generation of renewable energy. The concept of photocatalysis was first discovered by Eibner in 1911.$^{[1]}$ The new conceptualization of semiconductor-assisted photocatalysis has turned out to be the foundation for present-day solar fuel research. Artificial photosynthesis has been widely explored as it relies on solar energy, and it employs principles derived from natural photosynthesis. Consustancial to natural photosynthesis, solar-driven reduction of CO$_2$ into hydrocarbon fuels is a sustainable strategy for renewable energy production. Nevertheless, it is difficult to achieve high CO$_2$ conversion efficiency with the numerous limitations possessed by the existing designs of bulk-photocatalytic systems. To overcome these shortcomings, photocatalysts in the atomic dimension have been extensively researched due to the large surface-to-volume ratio and enhanced light-harvesting ability.$^{[2]}$ Downsizing photocatalysts into the atomic scale is an effective strategy to improve photocatalytic efficiency.

The recent progress in two-dimensional (2D)-related studies has sparked a surge of interest in exploring Aurivillius family semiconductors. Bi$_2$WO$_6$, the simplest member of the Aurivillius family, shows excellent potential in photocatalysis due to its high chemical stability, non-toxicity, and appropriate band position. However, the CH$_4$ yield from CO$_2$ photoreduction over pristine Bi$_2$WO$_6$ is relatively low, ascribed mainly to its sluggish charge-transport characteristics. Numerous attempts have been made to improve the photocatalytic performance of pristine Bi$_2$WO$_6$, including impurity doping, defect engineering, and heterojunction formation.$^{[3–6]}$

As widely accepted, incorporating non-metal elements can effectively enhance photocatalytic activity, owing to the improved electronic conductivity, creation of defects or active sites, and bandgap narrowing.$^{[7–9]}$ Sulfur (S) element has rarely been used as an anionic dopant for Bi$_2$WO$_6$, but research on S-doped Bi$_2$WO$_6$ is scarce. Herein, we describe the design of atomically thin Bi$_2$WO$_6$ decorated with S dopants for the photoreduction of CO$_2$. To the best of our knowledge, this is the first work that successfully incorporates foreign S atoms into Bi$_2$WO$_6$ atomic layers. The S loading is kept eminently low to avoid agglomeration as single atoms possess high surface energy.$^{[10]}$ S atoms have a range of accessible oxidation states and possess versatile redox ability in transition metal complexes.$^{[11]}$ Notably, atomically thin structures have low atomic-escape energy.$^{[12]}$ The bismuth atoms on the interface are coordinatively unsaturated sites and could potentially strengthen the photocatalytic properties as they expose a large...
number of active sites for redox reactions.\textsuperscript{[12]} The synthesis of atomically thin structures is highly challenging but highly desirable to improve the overall photoreduction of CO\textsubscript{2}.

**Results and Discussion**

Atomically thin pristine Bi\textsubscript{2}WO\textsubscript{6} (P-BWO) and S-doped Bi\textsubscript{2}WO\textsubscript{6} (S-BWO) nanosheets were synthesized through a hydrothermal process. As shown in Figure S1, the X-ray diffraction (XRD) peaks for both accumulated powder samples are ascribed to Bi\textsubscript{2}WO\textsubscript{6}, which crystallizes in the orthorhombic phase (JCPDS no. 73-1126). The XRD patterns of S-BWO are comparable to that of P-BWO, indicating that the crystal structure was not affected by the introduction of S element, due to the low S dopant content.\textsuperscript{[13,14]} The relative intensity of the peaks at the (200) plane to that of the (113) plane was calculated to be 0.813 for P-BWO and 0.825 for S-BWO, which is much higher than the standard ratio of 0.185. This elucidates that the prepared samples grow anisotropically along the [001] direction to predominantly expose the highly active (001) facets.\textsuperscript{[15]}

Moreover, the general morphology and microstructure of the atomically thin samples were investigated using transmission electron microscopy (TEM). Based on the high-resolution (HR)TEM image of P-BWO as shown in Figure 1a, two sets of crystal lattice fringes perpendicular to each other were measured to be 0.272 and 0.273 nm, which are ascribed to the (020) and (200) atomic planes, respectively.\textsuperscript{[16]} These findings confirm that the as-developed P-BWO nanosheets are predominantly exposed with (001) facets, as supported by the XRD analysis. For S-BWO, the HRTEM image in Figure 1b showed a slight increase in lattice spacing. Two sets of perpendicular lattice fringes with equal spacing of 0.275 nm were observed, corresponding to the (020) and (200) atomic planes. On another note, the lattice parameters of P-BWO were calculated to be \(a = 6.10\ \text{Å}, \quad b = 23.73\ \text{Å}, \quad \text{and} \quad c = 4.80\ \text{Å}\), whereas, for S-BWO, they were estimated to be \(a = 6.16\ \text{Å}, \quad b = 24.83\ \text{Å}, \quad \text{and} \quad c = 4.55\ \text{Å}\) based on density functional theory (DFT) calculations as shown in Table S2. The slight increase in lattice parameters is attributed to the substitution of O\textsuperscript{2-} anions (1.40 Å) with S\textsuperscript{2-} anions (1.84 Å) that have a bigger effective ionic radius. This theoretical calculation supports the HRTEM findings. Atomic force microscopic (AFM) imaging and the corresponding height profiles are presented in Figure 1c. It can be seen that the nanosheets have an average thickness of approximately 0.8 nm, which is in agreement with a unit cell thickness of Bi\textsubscript{2}WO\textsubscript{6}.\textsuperscript{[17]}

The surface chemical compositions of the synthesized catalysts were investigated by X-ray photoelectron spectroscopy (XPS). As delineated in Figure S2, the survey scan reveals Bi, W, and O elements in the sample. The C 1s peak discerned is from the charge correction prior to deconvolution. No foreign peaks were discovered, indicating that the samples are of high purity. As shown in Figure 2a, the two spin-orbit doublets with peaks emerging at 159.34 and 164.64 eV for P-BWO represent the photoelectrons of levels of Bi 4f\textsubscript{7/2} and Bi 4f\textsubscript{5/2}, implying the presence of Bi\textsuperscript{3+} chemical states. As for S-BWO, there is a slight reduction in the binding energy of 0.27 eV for both Bi 4f peaks at 159.07 and 164.37 eV due to the introduction of the S element into the crystal structure. With a shift to lower binding energy, it indicates that the electron density of S-BWO is higher than that in P-BWO. Besides, there is a noticeable S 2p peak at 165.44 eV that indicates the existence of S\textsuperscript{2-} species. Furthermore, the S 2s peak shown in Figure S2 confirms the existence of element S. The peak is relatively small due to the low loading amount of S. In regard to the W 4f spectrum for P-BWO as rendered in Figure 2b, the doublet peaks can be deconvoluted into binding energy of 35.61 and 37.73 eV, which are assigned to the W 4f\textsubscript{7/2} and W 4f\textsubscript{5/2} in the W\textsuperscript{6+} oxidation state of P-BWO. There is a 0.2 eV reduction in binding energy for both peaks of S-BWO, indicating that the chemical environment is altered with the introduction of the S element. As for the O 1s core spectrum, the deconvoluted peaks at 530.33 and 531.40 eV for P-BWO are attributed to lattice oxygen and surface chemisorbed oxygen, respectively. The binding energy for both peaks decreased by approximately 0.23 eV for S-BWO, as shown in Figure 2c. Furthermore, the lattice oxygen/bismuth ratio of P-BWO (0.168) is higher than that of S-BWO (0.154), indicating that S-BWO samples possess a more considerable amount of oxygen vacancies; thus, confirming that S\textsuperscript{2-} ions, with the same valency, have successfully substituted the O\textsuperscript{2-} ions in the lattice.

![Figure 1. HRTEM images of (a) P-BWO and (b) S-BWO. (c) AFM image and the corresponding height profiles of P-BWO.](image-url)
Moreover, energy-dispersive X-ray spectroscopy (EDX) mapping of S-BWO reaffirms the successful loading of S atoms onto the atomically thin nanosheets as depicted in Figure S3.

The optical properties of both P-BWO and S-BWO were studied using UV/Vis diffuse reflectance spectroscopy. As shown in Figure 2d, the absorption edge of S-BWO exhibits an obvious red-shift compared to that of P-BWO, indicating an increased absorption in the visible light region with the introduction of S. The red-shift is attributed to the charge-transfer transition between the electrons of the S\(^{2-}\) species and the CB of S-BWO. Based on the Tauc plots, the bandgaps of P-BWO and S-BWO were estimated to be 2.94 and 2.83 eV, respectively. The narrowing of bandgap increases the spectral range response to solar energy. It is worth noting that the bandgaps of the atomically thin samples are wider than Bi\(_2\)WO\(_6\) nanosheets, as depicted in Figure S4. The bandgap broadening of the atomically thin photocatalysts is a typical observation from quantum size effect,\(^{18}\) which further reaffirms the successful synthesis of Bi\(_2\)WO\(_6\) atomic layers.

The physicochemical properties of monolayer P-BWO and S-BWO were analyzed using first-principles DFT studies. The dopant formation energies were calculated to examine the most energetically favorable substitution site for S-BWO. The calculated formation energies for various possible O substitution sites are shown in Figure 3. The negative formation energies obtained indicate that the doping of these atomically thin structures can form spontaneously and therefore are the most probable substitution sites. The lower formation energy promotes the incorporation of impurity ions in the desired configuration. It is noted that the substitution of the S element in the Bi–O–Bi bond of the structure has the lowest formation energy, thus making it the most favorable doping position. In addition, the substituted energy value at the dangling Bi–O bond is also less than the formation energy of monolayer P-BWO, indicating that it may be a possible doping site. The formation energies calculated confirm that the substitutional doping of S ions into the O atom of Bi\(_2\)WO\(_6\) is thermodynamically favorable, which is consistent with the XPS results.

The photocatalytic performance of the atomically thin samples was evaluated by gas-phase photocatalytic reduction of CO\(_2\). A series of control experiments was performed in the absence of a water source, absence of a CO\(_2\) source, and without light illumination, respectively. As shown in Figure S5, no appreciable amounts of hydrocarbons were detected in all these cases, confirming that the CH\(_4\) product was formed via photocatalytic CO\(_2\) reduction and the possibility of self-photolysis and decomposition of carbon residuals can be confidently ruled out. Figure 4a shows the cumulative yield of CH\(_4\) from the photocatalytic reduction of CO\(_2\) under simulated solar irradiation for 6 h. S-BWO manifested an average CH\(_4\) yield of 7.33 μmol g\(^{-1}\), a 3-fold enhancement over the solitary monolayer P-BWO photocatalyst with a CH\(_4\) yield of 2.39 μmol g\(^{-1}\). The apparent quantum yield of S-BWO was calculated to be 0.023%. The superior performance of the developed S-BWO photocatalyst is ascribed to several concomitant factors. First, the presence of S led to an upward shift in conduction band (CB), which increased the reduction capability of S-BWO. The apparent CB potentials of P-BWO and S-BWO
were found to be $0.38$ and $0.46$ V vs. Ag/AgCl, respectively, based on the Mott-Schottky analysis as depicted in Figure 4b. The upward slopes shown in the Mott–Schottky plots are consistent with that of n-type semiconductors. For n-type semiconductors, the CB positions are approximately $0.2$ eV more negative than their flat-band potentials.\(^3\) According to Equation (1), the CB edges can then be estimated to be $-0.38$ and $-0.46$ V vs. normal hydrogen electrode (NHE), respectively:

$$E_{\text{NHE}} = E_{\text{Ag}/\text{AgCl}} + 0.1976$$  \(1\)

Finally, the valence band (VB) positions of P-BWO and S-BWO were then calculated to be $2.56$ and $2.37$ V, respectively. The energy band diagrams are illustrated in Figure S6. The elevation of CB increases the reduction capability of the photocatalyst by generating more reductive photoexcited electrons, which is advantageous for CO\(_2\) photoreduction. To evaluate the stability of the photocatalysts, three consecutive test cycles of CO\(_2\) reduction were performed under identical experimental conditions, as illustrated in Figure S7. Intriguingly, S-BWO exhibited superior photostability as compared to P-BWO, retaining 90% of its reactivity. This indicates that S-BWO

Figure 3. Formation energies of P-BWO and various doping sites of S-BWO; red: O, grey: W, purple: Bi, yellow: S.

Figure 4. (a) Rate of CH\(_4\) production with P-BWO and S-BWO for 6 h under simulated sunlight irradiation. (b) Mott-Schottky curves, (c) Nyquist plots, (d) transient photocurrent responses, (e) TRPL decay curves, and (f) PL spectra of P-BWO and S-BWO.
is well suited for practical applications of solar energy conversion.

To further disclose the mechanistic properties of the photocatalysts, Nyquist plots of the samples were investigated. As shown in Figure 4c, S-BWO displayed a smaller arc radius as compared to that of P-BWO. Generally, a smaller arc radius represents a lower electron transfer resistance, thus indicating a higher efficiency of interfacial charge transfer for S-BWO. As a result, the separation and migration of charge carriers of S-BWO are promoted. This is in good agreement with the transient photocurrent density of the samples that was examined through on-off cycles of intermittent visible light irradiation, as seen in Figure 4d. In particular, a pronounced enhancement in the photocurrent intensity of S-BWO was observed, indicating a higher efficiency of generation and separation of photogenerated charge carriers, as well as the retarding of electron-hole pairs recombination rate. The results from the transient photocurrent responses are consistent with the CO$_2$ reduction results. Furthermore, time-resolved photoluminescence (TRPL) and photoluminescence (PL) studies were conducted to provide an insight into the dynamics and lifetime of the charge carriers. The TRPL decay curves are illustrated in Figure 4e. The average emission lifetime increases from 0.56 to 1.31 ns with the incorporation of S. It is evident that the incorporation of S element has prolonged the lifetime of the photogenerated charge carriers. Similar results have been obtained in the PL spectra of the samples. The weaker emission peak of S-BWO as shown in Figure 4f represents an improved suppression of the electron-hole pair recombination. The enhanced separation efficiency and prolonged lifetime of photogenerated charge carriers caused by S doping are beneficial for improving photocatalytic activity.

Density of states (DOS) analysis was obtained from DFT and plotted as shown in Figure 5a,b. For P-BWO, it can be noted that the VB consists mainly of O 2p orbital, whereas the bottom of the CB is originated from Bi 6p, O 2p, and W 5d orbitals. Figure 5b shows that the bottom of the CB for S-BWO was attributed to the hybridization of W 5d, O 2p, Bi 6p, and S 3p orbitals. The formation of a new hybridized state upon S doping upshifted the energy levels of the VB, resulting in narrowing of bandgap. The narrowing of bandgap can extend the photoresponsiveness as well as decreasing the electron transition energies. Moreover, the Fermi level ($E_F$) of S-BWO has shifted towards the CB concomitant to the narrowing of bandgap, indicating a greater electron density in the system. Work function (WF) quantifies the minimum energy required for an electron to transition from the $E_F$ to the vacuum energy level. By doping with S, the $E_F$ shifted closer to the CB as the probability of encountering free electrons increased, which concurs with the DOS plot. The shifting of the $E_F$ relative to the WF as obtained from DFT simulations is illustrated in Figure 5c,d. The calculated WF of S-BWO (8.58 eV) is 0.36 eV lower than that of P-BWO (8.94 eV). This reduction in WF enables more electrons to escape, thus resulting in an increase in charge carriers participating in the reaction.

The adsorption energies of the interaction between CO$_2$ and P-BWO and S-BWO are calculated to be $-162.57$ and $-164.51$ eV, respectively. This shows that the doping of S could promote the adsorption of CO$_2$ onto atomically thin Bi$_2$WO$_6$. This is in agreement with the experimental results obtained.
from CO₂ adsorption isotherm analysis, as shown in Figure S8. Notably, S-BWO exhibited higher adsorption capacities for CO₂ as compared to P-BWO.

To further illustrate the effect of S atoms doping on the redistribution of charge, the charge density difference for P-BWO and S-BWO of the most favorable doping site was performed. The electron density difference displayed in Figure 6a shows that there is charge accumulation around the S atom. On the contrary, the S atom became the charge depletion region after interacting with CO₂. This phenomenon indicates a greater amount of charge transfer between the S atom and CO₂, which explains the higher CO₂ adsorption energy and better attraction of CO₂ to S-BWO than that of P-BWO. Moreover, CO₂ has a greater bond bending with S-BWO as compared to P-BWO, as shown in Figure S9. Notably, bending the molecule from its linear equilibrium geometry reduces its lowest unoccupied molecular orbital energy, which makes the molecule electrophilic.[21] The more reactive bent form facilitates the electron transfer process, which turns CO₂ into a radical anion, increasing its reactivity with the catalyst. It is also worth noting that the bond length between CO₂ and S-BWO is smaller as compared to P-BWO, indicating that CO₂ is better adsorbed onto the S atom of the doped catalyst, as depicted in Figure S9.

The free energy diagrams of each intermediate system for CO₂ reduction are obtained by DFT calculations and shown in Figure 6b. The thermodynamic profile indicates that the potential determining step is the activation of CO₂ molecule. The CO₂ molecule is first hydrogenated through a proton-electron transfer step, resulting in an O–H bond formation to produce a *COOH intermediate. The activation of CO₂ is an endothermic process as CO₂ is chemically inert and a very stable molecule. The free energy differences of P-BWO and S-BWO are 1.52 and 1.38 eV, respectively. Specifically, S-BWO exhibits a lower free energy difference value, suggesting its high activity for the conversion of CO₂ to *COOH. The *COOH intermediate was subsequently transformed to *HCOOH and *HCO. The *HCO is then hydrogenated to *CH₂O, *CH₃O, and finally reduced to CH₄. For S-BWO, it can be seen that the free energy differences for each intermediate step are lower as compared to P-BWO, indicating that it is more favorable for CO₂ reduction to CH₄.

**Conclusion**

We have developed atomically thin BiₓWO₆ nanosheets with an average thickness of 0.8 nm via a bottom-up approach. Foreign atoms doping has been demonstrated as an effective strategy to tune the electronic properties of a semiconductor. The CO₂ reduction activity of S-BWO exhibited a 3-fold improvement as compared to P-BWO. The remarkable enhancement is attributed to the enhanced reduction ability due to the regulated band structure, extended visible light absorption, efficient separation of charge carriers with a lower electron transfer resistance, and a longer lifetime of charge carriers. Due to the atomically thin nature of BiₓWO₆, the surface atoms are coordinately unsaturated exposing a huge number of active sites. Density functional theory calculations revealed that the addition of S atoms not only enhanced the adsorption of CO₂ but the work function of S-BWO was also reduced, enabling more electrons to be transferred to the adsorbed CO₂; hence, resulting in superior photocatalytic performance. The findings in this work undoubtedly open up new paths to further advance photocatalytic systems through charge modulation at an atomic scale.

**Experimental Section**

**Chemicals**

Bismuth(III) nitrate pentahydrate powder [Bi(NO₃)₃·5H₂O] with an assay ≥ 98.0 %, cetyltrimethylammonium bromide [CTAB, CH₃(CH₂)ₙN(Br)(CH₂)ₙ] with an assay ≥ 99.0 %, and thiourea (NH₂CSNH₂) with an assay ≥ 99.0 % were supplied by Sigma Aldrich. Sodium tungstate dihydrate powder (Na₂WO₄·2H₂O) with an assay ≥ 99.0 % was procured from Merck. All reagents were of analytical grade and used without further purification. Deionized water with a resistivity ≥ 18.2 MΩ cm was utilized throughout the experiment.

![Figure 6](image-url). (a) Charge density differences of (i) P-BWO, (ii) S-BWO, (iii) CO₂-adsorbed P-BWO, and (iv) CO₂-adsorbed S-BWO. The red region denotes the greatest charge accumulation, whereas the blue region indicates greatest charge depletion. (b) Free energy profiles of P-BWO and S-BWO.
Synthesis of atomically thin Bi$_2$WO$_6$ nanosheets

Atomically thin Bi$_2$WO$_6$ nanosheets (P-BWO) were synthesized through a one-pot hydrothermal process, where CTAB was employed as a capping agent. In brief, 2 mmol of Bi(NO$_3$)$_3$·5H$_2$O was dissolved in 70 mL of deionized water (Solution A). Then, 1 mmol of Na$_2$WO$_4$·2H$_2$O and 0.14 mmol of CTAB were dissolved in 10 mL of deionized water under constant magnetic stirring (Solution B). Subsequently, Solution B was added to Solution A, and the mixture was stirred for 1 h in ambient temperature and pressure. The mixture was then poured into a Teflon-sealed autoclave with a capacity of 100 mL, heated to 120 °C, and maintained at this temperature for 24 h. After cooling to room temperature naturally, the formed precipitate was filtered and washed with deionized water several times. Finally, the collected precipitate was dried in a vacuum oven at 60 °C overnight. The synthesis procedure for S-BWO was similar to that of P-BWO except that 0.5 mmol of thiourea was added into Solution B.

Materials characterization

The synthesized samples were observed under Hitachi SU8010 field emission scanning electron microscopy (FE-SEM) and the EDX mapping of the samples was then acquired. HRTEM images were acquired using Tecnai G2 F20 transmission electron microscope at an accelerating voltage of 200 kV. The crystal phase of the samples was measured by Bruker D8 Discover XRD. XPS was also performed using a scanning X-ray microprobe PHI Quantera II (ULvac PHI, INC) to study the elemental composition of the photocatalyst. A charge correction with reference to the C–C peak at 284.6 eV from the C 1s spectra was applied to all binding energies to ensure that the results are calibrated and accurate. The C–C peak of the C 1s was selected as a reference because most samples will have a layer of adventitious carbon contamination of 1 to 2 nm thick once they are exposed to the atmosphere. TRPL spectra were acquired using a DeltaPro fluorescence lifetime system (Horiba Scientific) with an excitation wavelength of 415 nm. Agilent Cary 100 UV/Vis spectrophotometer was utilized to obtain the absorbance spectra of the samples.

Electrochemical analysis

The electrochemical measurements were carried out by a CHI 600SE electrochemical workstation with a conventional three-electrode quartz cell. The as-prepared samples were spray-coated on a fluorine-doped tin oxide (FTO) substrate with an active area of 1 cm$^2$ and utilized as the working electrode. Ag/AgCl saturated with 3 M KCl served as the reference electrode with Pt as the counter electrode. The electrolyte used was 0.5 M Na$_2$SO$_4$ solution. The working electrode was irradiated with a 500 W Xe arc lamp (CHF-XM-500W) equipped with a UV cut-off filter to simulate visible light (λ > 400 nm).

Evaluation of photocatalytic activity

The photocatalytic activities of the synthesized samples were measured by CH4 photoreduction into CH$_2$. The experiment was conducted at room temperature and at atmospheric pressure in a continuous gas flow reactor. A 500 W Xenon arc lamp (CHF-XM-500W) was equipped with an AM1.5 cut-off filter to simulate solar light. For the set-up of the experiment, the photocatalysts were uniformly coated onto glass rods and were placed into their respective quartz columns. To omit any external light interference, the columns were placed in an enclosed black box where the loaded quartz columns were hatched onto the quartz holder rigidly to prevent movement of the quartz column throughout the experiment. CO$_2$ gas of high purity (99.999%) was bubbled through liquid water to provide CO$_2$/H$_2$O mixture in gas phase and was introduced into the system as the reactant gas. Prior to the photocatalytic experiment, the CO$_2$/H$_2$O gas mixture was purified through the reactor at a flow rate of 50 mL min$^{-1}$ for 30 min to ensure that the reactant gas molecules were completely adsorbed on the surface of the photocatalysts and to remove any contaminants from the column. Subsequently, the CO$_2$/H$_2$O gas flow rate was adjusted to 5 mL min$^{-1}$ for 6 h under visible light irradiation. A gas chromatography (Agilent 7820A GC), equipped with flame ionized detector (FID) and thermal conductivity detector (TCD), was then utilized to quantify and analyze the components of the product gas in hourly intervals. The total CH$_4$ yield was quantified using the following Equation (2):

$$\text{CH}_4 \text{ yield (} \mu\text{mol g}^{-1} \text{)} = \frac{\text{total amount of CH}_4 \text{ produced (} \mu\text{mol)}}{\text{mass of photocatalyst used (g)}}$$

The apparent quantum yield (AQY) is defined as the ratio of number of reacted electrons to the number of incident photons. Stoichiometrically, 8 electrons are required to produce one molecule of CH$_4$. Hence, the AQY for CH$_4$ evolution was calculated using the following Equation (3):

$$\text{AQY} \text{ [%] } = \frac{\text{number of reacted electrons}}{\text{number of incident photons}} \times 100 \% = \frac{8 \times \text{number of CH}_4 \text{ produced}}{\frac{8 \times [\text{CH}_4] \times N_A}{I / S (\pi)} \times 100 \%}$$

where [CH$_4$] represents the mole of CH$_4$ produced in time t, t is reaction time [s], $N_A$ is Avogradro’s constant of 6.0221 × 10$^{23}$ mol$^{-1}$, I is intensity of incident light [W cm$^{-2}$], $\lambda$ is the wavelength of incident light [nm], S is irradiation area [cm$^2$], h is Planck’s constant of 6.6261 × 10$^{-34}$ J s, and c is speed of light, which is 3 × 10$^8$ m s$^{-1}$.

Computational details

The first-principles DFT calculations were carried out with the Vienna ab initio simulation package (VASP). In the cases of CO$_2$ adsorption, long range Van der Waals interactions were taken into consideration using DFT-D3 approach with Grimme correction. All models (2 × 2 × 1) were repeated periodically in the x–y plane and separated in the z-direction with a 15 Å vacuum region to avoid spurious interactions between periodic slabs. A 2 × 2 × 1 Monkhorst-Pack k-point grid was adopted to sample the Brillouin zone. The plane-wave cutoff energy of 500 eV, ionic relaxations were carried out under conventional energy (1 meV atom$^{-1}$) and Hellmann–Feynman force (0.01 eVÅ$^{-1}$) convergence criteria. All calculations are performed with non-spin polarization. The Gibbs free energy change, $\Delta G$, was defined as shown in Equation (4):

$$\Delta G = \Delta E + \Delta E_{\text{PE}} - T \Delta S$$

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where $\Delta E$ is the change in reaction energy determined from DFT total energies of the system, $\Delta E_{ZPE}$ is the change in zero-point energy, and $\Delta S$ is the change in entropy of the adsorbed species at the reference temperature 298.15 K taken from the NIST database (refer to Table S3).\[39\]

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**Conflict of Interest**

The authors declare no conflict of interest.

**Data Availability Statement**

The data that support the findings of this study are available from the corresponding author upon reasonable request.

**Keywords:** CO$_2$ reduction · density functional theory · nanosheets · photocatalysis · sulfur doping

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