



Research article

Sulfur-doping-engineered compressive strain promotes interlayer charge transport for efficient CO₂ photoreduction in bismuth oxyhalidesKangjie Gao^a, Yuanyuan Zhao^b, Huanhuan Liu^{a,*}, Jiaxin Li^b, Peisen Luo^b, Fang Chen^{c,*}, Wentao Wang^{d,*}, Yong Hu^{a,*}^a Institute of Nanocatalysis and Energy Conversion, Zhejiang Key Laboratory of Green and Low-Carbon Utilization Technology of Agricultural and Forestry Biomass, College of Chemistry and Materials Engineering, Zhejiang A&F University, Hangzhou 311300, China^b Key Laboratory of the Ministry of Education for Advanced Catalysis Materials, Zhejiang Key Laboratory of Advanced Catalysis and Adsorption Materials, Department of Chemistry, Zhejiang Normal University, Jinhua 321004, China^c Hangzhou Institute of Advanced Studies, Zhejiang Normal University, Hangzhou 311231, China^d Guizhou Provincial Key Laboratory of Computational Nano-Material Science, Guizhou Education University, Guiyang 550018, China

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ABSTRACT

Solar-driven CO₂ photoreduction offers a compelling route to carbon neutrality, but its efficiency is limited by sluggish charge separation and a high CO₂ activation barrier. Conventional strategies like heterojunction construction and point-defect engineering are often hampered by the trade-off between bulk charge transport and surface reaction kinetics, or by lattice instability. Herein, we overcome these kinetic bottlenecks through a doping-driven interlayer strain engineering strategy that induces long-range ordered lattice distortion in two-dimensional bismuth oxyhalides (BiOX, X=Cl, Br, I). Controlled sulfur substitution at oxygen sites introduces localized compressive strain along the [0 0 1] direction, which reduces the van der Waals interlayer spacing. This structural modulation leads to a 4.69-fold amplification of the built-in electric field, establishing a rapid vertical charge-transport pathway that accelerates carrier separation. Concurrently, the compressive strain shifts the p-band center of Bi sites upward, strengthening Bi-6p/CO₂-2π* orbital hybridization and thereby promoting CO₂ chemisorption and activation. The synergy between accelerated charge dynamics and optimized surface electronic structure lowers the barrier for *COOH formation, enabling highly selective CO production. As a result, the optimized S-doped BiOBr catalyst achieves a CO evolution rate of 81.34 μmol g⁻¹ h⁻¹ without sacrificial agents, representing a 9.53-fold enhancement over pristine BiOBr and surpassing other BiOX variants. This work validates interlayer strain engineering as a general strategy to unlock the catalytic potential of layered materials for efficient CO₂ conversion.

1. Introduction

The rapid pace of industrialization and urbanization has led to a sharp increase in carbon dioxide (CO₂) emissions from fossil fuel consumption, exacerbating the greenhouse effect and climate change, thereby posing a major threat to global sustainability [1,2]. Converting CO₂ into carbon monoxide (CO) not only mitigates the levels of greenhouse gases in the atmosphere but also produces a valuable feedstock for processes such as the water–gas shift reaction and the Fischer–Tropsch process [3,4]. Photocatalytic CO₂ reduction (PCR) technology, which

harnesses clean energy under ambient conditions, provides an attractive approach for targeted CO₂-to-CO conversion [5]. Nevertheless, the rapid photogenerated charge recombination dynamics of photocatalysts significantly restricts the catalytic efficiency, thereby imposing constraints on large-scale application in the industry [6]. Regulating lattice distortion within the photocatalyst has emerged as an effective strategy for enhancing the efficiency of CO₂ reduction [7,8]. By intentionally modifying the atomic arrangement and local electronic structure, such controlled structural perturbation can strengthen built-in electric fields and promote the spatial separation of photogenerated electrons and

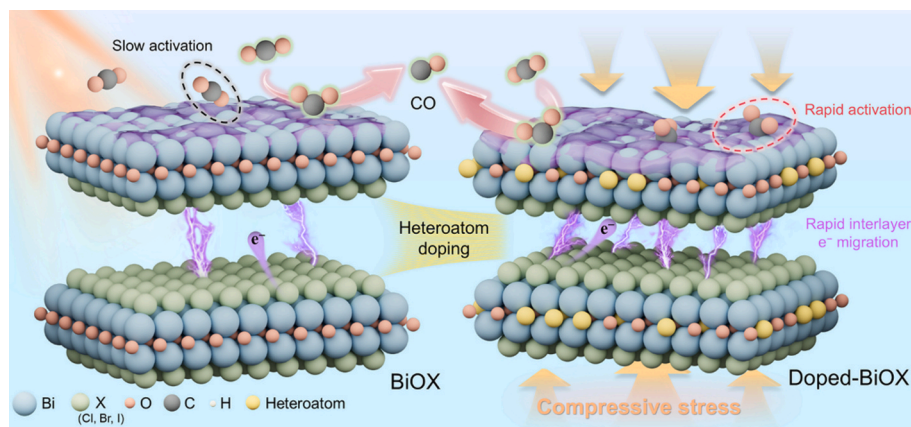
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Scheme 1. Doping-driven strain engineering for optimizing layered photocatalysts. Taking BiOBr as an illustrative example, S-doping introduces compressive strain that reduces the interlayer spacing, thereby providing a rapid vertical electron channel. This structural modification significantly enhances charge separation efficiency and suppresses bulk recombination, ultimately increasing electron density at the reduction site and promoting CO₂ adsorption and activation.

holes [9].

However, despite its immense potential, the effective implementation of lattice distortion engineering typically faces significant challenges [10]. Conventional methods predominantly induce distortion at the point-defect scale (0D), for instance, by generating vacancies or interstitial atoms [11]. This spatially confined modification resulted in inherent limitations: the random distribution of point defects renders it arduous to attain uniform and predictable structural changes, and these localized perturbations frequently act as recombination centers themselves, unexpectedly trapping charges [12]. Furthermore, the generation and stabilization of these point defects typically necessitate intricate, high-energy procedures (such as high-temperature annealing, ion bombardment, or exposure to reactive plasmas), which not only increases the complexity and cost but also presents a risk of uncontrolled structural deterioration [7]. In stark contrast, layered materials define their structural anisotropy through the interplay of strong in-plane covalent bonds and weak interlayer interactions, providing a unique platform for strain accommodation and propagation [13]. Within layered materials, random point strains are transformed into long-range ordered strain fields or even controlled lattice distortions, such as interlayer spacing modulation and the formation of twisted domains [14,15]. By capitalizing on this interlayer dimension, the distortion mechanism is elevated from isolated 0D points to a coherent 2D plane, thereby significantly expanding the spatial extent and efficacy of the structural perturbation across the entire material [7]. Consequently, the challenge lies in transforming its application from the generation of random 0D point defects to the deliberate design of strain fields.

As a typical layered compound, bismuth oxyhalides (BiOX, X = Cl, Br, or I) are composed of [Bi₂O₂] layers and [X] layers, where the [Bi₂O₂] layers, constituted by Bi and O atoms through strong covalent bonding, interact with the [X] layers via van der Waals forces. The electrostatic potential difference existing between the [Bi₂O₂] layers and [X] layers gives rise to a robust built-in electric field for directing photogenerated electrons and holes to the {0 0 1} and {2 0 0} crystal planes, respectively, which enables efficient charge separation and facilitates the transfer of charges from the bulk to the surface [16,17]. However, the weak interlayer van der Waals interactions result in suppressed photoinduced electron migration dynamics along the {0 0 1} surface, therefore inhibiting the photoreduction performance [18]. Currently, the photocatalytic performance of BiOX can be improved through various optimization measures, such as thickness reduction, heterojunction construction, and interface engineering [19,20]. However, the inherent issues of sluggish carrier mobility and severe charge recombination on the {0 0 1} surface remain unresolved [21]. Structural distortion engineering to reduce the interlayer spacing of the BiOX {0 0 1} surface is a promising approach for accelerating carrier migration.

Nevertheless, conventional strain engineering approaches of BiOX typically depend on intricate synthesis schemes that demand precise manipulation of external stimuli or multi-step heterostructure assembly processes [22,23].

Unfortunately, these strategies are hampered by interfacial incompatibility, limited strain tunability, and complex synthesis, which hinder their practical application in large-scale photocatalyst design [24,25]. In this context, elemental doping offers a direct and efficient route to generate a localized strain field [26]. By leveraging the mismatch in atomic radius between host and dopant atoms, doping modulates both the electronic and geometric structure of the material. This targeted strain engineering maintains material integrity and permits atomic-scale control of strain distribution, which is essential for optimizing charge transport and increasing active site accessibility. Therefore, to improve PCR, we aimed to facilitate charge transport by compressing the BiOX (0 0 1) interlayer spacing. We selected sulfur (S) to substitute for lattice oxygen, leveraging its distinct atomic size and electronegativity to generate localized compressive strain and tailor the electron density around Bi sites, thereby enhancing CO₂ adsorption and activation (Scheme 1). Within the BiOX family, BiOBr was chosen as the optimal host material due to its superior balance of structural stability and tunability compared to BiOCl [21]. In contrast, BiOI, with its larger innate interlayer spacing and weak interlayer forces, is prone to structural relaxation or collapse under strain-inducing doping [27]. As anticipated, the resulting S-doped BiOBr nanosheets (S-BiOBr NSs) exhibit significant compressive strain along the [0 0 1] direction, which effectively accelerates interlayer charge separation. Crucially, the optimized electronic structure features an upshifted Bi p-band center and enriched local electron density. This modulation reduces the energy offset between the Bi-6p and CO₂-2π* orbitals, thereby enhancing CO₂ adsorption and improving the kinetics and thermodynamics of its photoreduction. The synergy between accelerated interlayer charge migration and this optimized surface electronic structure establishes a comprehensive strategy for overcoming key kinetic limitations in PCR. Consequently, the S-BiOBr-2 sample achieves the highest CO₂ reduction efficiency (81.34 μmol g⁻¹ h⁻¹), which is approximately 9.53 times greater than that of pristine BiOBr.

2. Experimental section

2.1. Materials

Sinopharm Chemical Reagents Co., Ltd. (China) supplied the analytical-grade thiourea, alongside the potassium halides including potassium iodide (KI), potassium chloride (KCl), and potassium bromide (KBr). Meanwhile, anhydrous bismuth nitrate (Bi(NO₃)₃) and ethylene

glycol (EG) of analytical purity were procured from Aladdin Chemical Reagents Co., Ltd. (China). All acquired reagents were applied directly as received without any additional purification steps, and deionized (DI) water functioned as the universal solvent for all experimental procedures.

2.2. Synthesis of the S-BiOBr and BiOBr NSs

S-BiOBr NSs were synthesized via a simple hydrothermal method as described below: 0.395 g of $\text{Bi}(\text{NO}_3)_3$ was dissolved in 5 mL of EG to form a homogeneous mixed solution. Subsequently, this solution was added to a 30 mL aqueous solution containing 0.12 g of KBr and thiourea, resulting in an ivory-white solution, and then stirred for 20 min. Next, the entire obtained suspension was transferred to a 50 mL autoclave and maintained in an oven at 160 °C for 12 h. After the mixture cooled to room temperature, the resulting precipitate was washed three times with deionized water and dried overnight in a vacuum oven at 80 °C. The final products were designated as S-BiOBr- x ($x = 1, 2$, and 3) NSs, corresponding to the addition of 5, 10, and 15 mg of thiourea, respectively. Regarding the BiOBr NSs, the preparation method is highly analogous to that of S-BiOBr NSs, except that thiourea is not added.

2.3. Synthesis of the S-BiOCl and S-BiOI NSs

For the S-BiOCl and S-BiOI NSs, the preparation method was analogous to that used for S-BiOBr NSs, with KBr being replaced with KCl or KI while maintaining the molar ratio of halogen atoms. The resulting products are denoted as S-BiOCl and S-BiOI, corresponding to the same sulfur doping level as that of S-BiOBr-2.

2.4. Materials characterization

To observe the microstructural features and elemental makeup of the materials, field-emission scanning electron microscopy (FESEM) was conducted utilizing a GeminiSEM 300 analyzer (Japan) operating at 5 kV. Concurrently, transmission electron microscopy (TEM), high-resolution TEM (HRTEM), and selected-area electron diffraction (SAED) were carried out on a JEOL JEM-2100F system (Japan) with an accelerating voltage of 200 kV. The topographic thickness of the prepared samples was determined via an Oxford MFP-3D atomic force microscope (AFM). For crystal phase identification, powder X-ray diffraction (XRD) patterns were recorded at a scan rate of $0.06^\circ \text{ s}^{-1}$ on a German Philips PW 3040/60 diffractometer equipped with a $\text{Cu K}\alpha$ radiation source. Bulk elemental quantification was achieved using an Elementar Vario EL Cube analyzer. To elucidate the surface chemical states, X-ray photoelectron spectroscopy (XPS) was executed on a UK-sourced ESCALab MKII spectrometer (Al $\text{K}\alpha$ excitation), utilizing a 20 eV pass energy and a 0.05 eV step size. The characteristic Bismuth (Bi) $\text{K}\alpha$ emission lines were monitored via a laboratory-scale X-ray emission spectrometer (XEScope, Anhui Absorption Spectroscopy Analysis Instrument Co., Ltd.). Optical absorption properties were evaluated by UV-Vis diffuse reflectance spectroscopy (DRS) using a Japanese Thermo Nicolet Evolution 500 spectrophotometer coupled with an integrating sphere. Structural vibrations were probed with a LabRAM HR Evolution Raman spectrometer (UK) under 532 nm laser excitation. Isotope-tracing investigations were performed under identical photocatalytic conditions by substituting $^{13}\text{CO}_2$ with $^{12}\text{CO}_2$. A 0.1 mL gas sample was extracted via a gastight syringe for subsequent analysis on a USA-made Agilent 6890 N GC instrument interfaced with an Agilent 5975B inert XL MSD. The surface photovoltage (SPV) spectra were recorded using a homemade apparatus (PL-SPV/IPCE1000 Beijing Perfect light Co., Ltd. China), which consist of a monochromatic light source, a light chopper (SR 540, Stanford research, Inc.), and a lock-in amplifier. Dynamic surface intermediate tracking was recorded using in-situ DRIFTS on a Bruker INVENIO FTIR spectrometer (Germany) utilizing a liquid nitrogen-cooled MCT detector. Experimentally, the catalysts were pre-

treated in a 30 mL min^{-1} Ar flow at 120 °C for half an hour to remove surface contaminants. Following this, the chamber was cooled to room temperature and fed with a gaseous mixture of Ar (25 mL min^{-1}), CO_2 (5 mL min^{-1}), and a trace amount of moisture. Once adsorption saturation was achieved (around 30 min), FTIR spectra were continuously captured under both dark and illuminated conditions over varying time intervals. The CO_2 desorption behaviors were monitored through temperature-programmed desorption (TPD) with a Micromeritics Autochem II 2920 (USA). Finally, the specific surface area and textural porosities were evaluated at 77 K based on the Brunauer-Emmett-Teller (BET) method utilizing a Micromeritics ASAP 2460 analyzer.

2.5. Photo-electrochemical measurements

To fabricate the working electrode, a homogeneous slurry was formulated by dispersing 5 mg of the solid sample into a solvent mixture comprising 50 μL of ethanol, 30 μL of ethylene glycol, and 10 μL of Nafion ionomer. Subsequently, 8 μL of this suspension was drop-casted onto a designated $1 \times 1 \text{ cm}^2$ area of an FTO conductive glass substrate, followed by desiccation in a 60 °C oven. All electrochemical investigations, encompassing photocurrent responses, open-circuit potential (OCP), Mott-Schottky (M-S) analysis, electrochemical impedance spectroscopy (EIS), linear sweep voltammetry (LSV), and differential pulse voltammetry (DPV), were executed using a CHI 660E workstation (China). The analyses were conducted in a conventional three-terminal cell configuration containing 0.5 M aqueous Na_2SO_4 as the supporting electrolyte. An Ag/AgCl electrode and a $1 \times 1 \text{ cm}^2$ platinum plate functioned as the reference and auxiliary electrodes, respectively. During the specific tests, M-S profiling was recorded across varying applied biases at discrete frequencies of 1200, 1400, and 1600 Hz. For EIS, an alternating current (AC) amplitude of 0.3 V was applied over a frequency sweep from 100 kHz down to 0.1 Hz. The OCP was monitored continuously for a duration of 400 s. Furthermore, LSV curves were traced from 1 V to -1 V at a sweep velocity of 0.02 V s^{-1} , while DPV scans were programmed within a potential window ranging from 0 V to -1 V.

2.6. Photocatalytic performance tests

The evaluation of CO_2 photoreduction performance was carried out in a Pyrex reactor connected to a Labsolar-6A gas-circulation system (Beijing Perfectlight, China). For the preparation of the test sample, 5 mg of the photocatalyst was ultrasonically dispersed in 2 mL of DI water for half an hour. The resulting uniform suspension was then drop-cast onto a circular fiberglass membrane (4 cm in diameter) and allowed to dry under ambient conditions. Subsequently, the catalyst-loaded membrane was mounted on a tripod inside the reactor, with 2 mL of DI water placed at the reactor's base to provide moisture. Prior to irradiation, the sealed chamber underwent three continuous cycles of evacuation and refilling with ultrapure CO_2 ($\geq 99.999\%$) until the internal pressure reached approximately 80 kPa. A 300 W Xenon arc lamp (Beijing Perfectlight, China) served as the incident light source, while the entire reactor was shielded with aluminum foil to eliminate any stray light interference. The system temperature was strictly regulated at 25 °C via a circulating water. Evolved reaction products were sampled hourly and quantified using an online gas chromatograph (Shimadzu GC-2014, Japan) configured with argon as the carrier gas, alongside FID and TCD detectors. For precise O_2 determination, the initial background air remaining in the system was recorded as a baseline, which was systematically subtracted from all subsequent oxygen measurements.

The incident light intensity reaching the catalyst surface was measured using an optical power meter (ST-85, Beijing Normal University Photoelectric Technology Co. LTD, China). The average value of light intensity ($\bar{I}_{\text{ave}}$) calculated by Eq. (1) is 258.5 mW cm^{-2} for the full-spectrum light resource. The $\bar{I}$ is 6.5, 28.9, 32.7, 42.3, and 53.2 mW

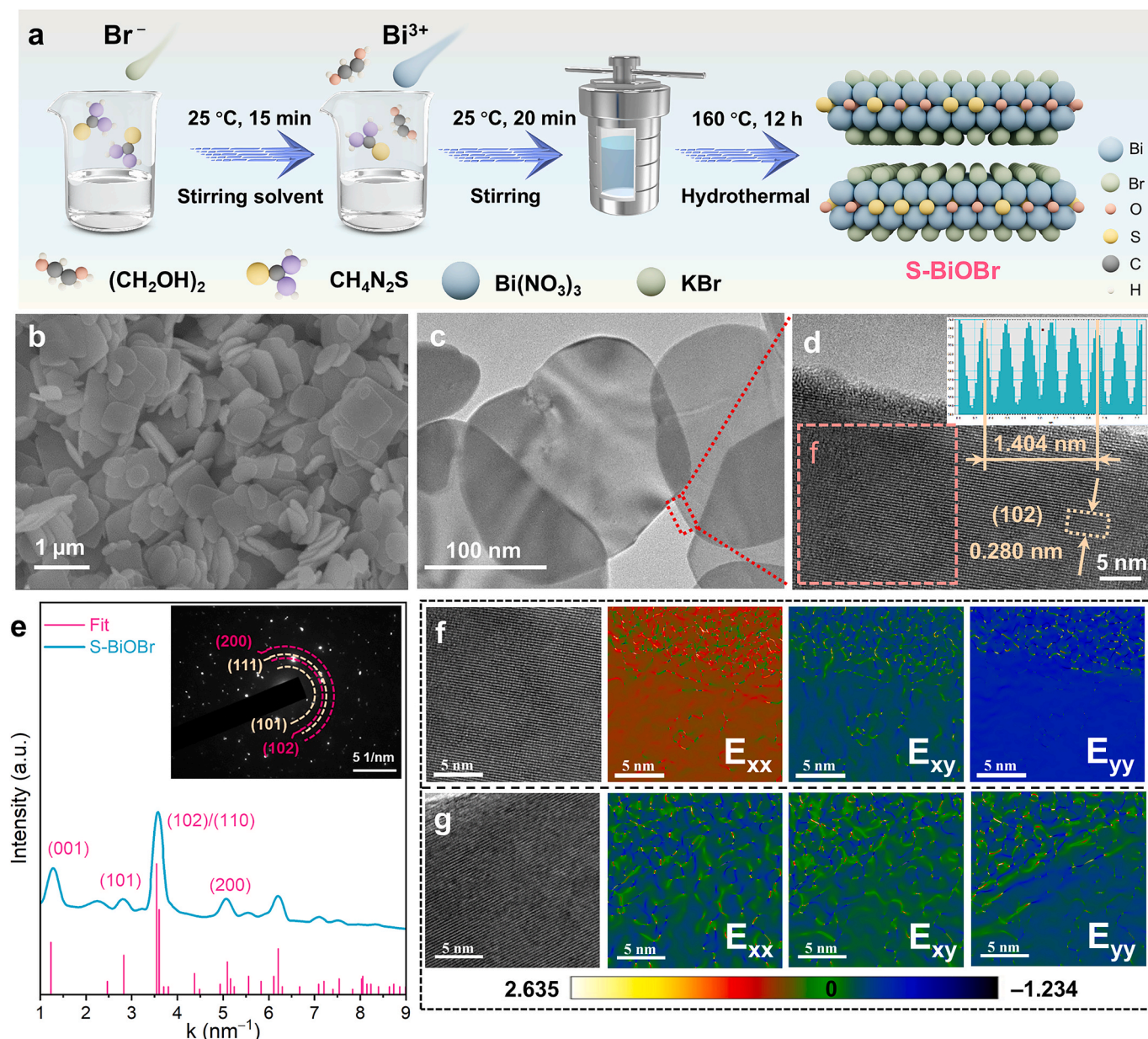


Fig. 1. (a) Schematic illustration of the synthetic process of S-BiOBr NSs. (b) FESEM, (c) TEM, and (d) HRTEM images of S-BiOBr-2 NSs. (e) Averaged diffraction ring positions and intensities from the SAED pattern (inset) of S-BiOBr-2 NSs. Strain maps along the xx, xy, and yy directions of the selected regions from (f) S-BiOBr-2 and (g) BiOBr NSs, determined via GPA.

cm^{-2} at 400, 420, 450, 500, and 550 nm, respectively.

$$\bar{I}_{\text{ave}} = \frac{2}{3}\bar{I}_{\text{edge}} + \frac{1}{3}\bar{I}_{\text{center}} \quad (1)$$

where $\bar{I}_{\text{edge}}$ and $\bar{I}_{\text{center}}$ correspond to the mean illumination intensities measured in the boundary and central zones, respectively, and the corresponding measured areas are shown in Fig. S1. Furthermore, the apparent quantum yield (AQY) for CO production was evaluated according to Eq. (2):

$$\begin{aligned} \text{AQY} &= \frac{2 \times \text{Number of evolved CO molecules}}{\text{Number of incident photons}} \times 100\% \\ &= \frac{2 \times N \times N_A \times h \times c}{\bar{I} \times S \times \lambda \times t} \times 100\% \end{aligned} \quad (2)$$

where N is CO evolution amount (mol), t is the irradiation time (s), λ is the irradiation wavelength number (m), N_A is the Avogadro constant

($6.022 \times 10^{23} \text{ mol}^{-1}$), S is the irradiation area (cm^2), h is the Planck constant ($6.63 \times 10^{-34} \text{ J}\cdot\text{s}$), and c is the light speed ($3 \times 10^8 \text{ m s}^{-1}$).

2.7. Density functional theory (DFT) calculation

Details of the DFT calculation are provided in the [Supplementary Information](#).

3. Results and discussion

3.1. Morphological and structural characteristics

As depicted in Fig. 1a, S-BiOBr-2 NSs were synthesized through a simple hydrothermal method. The FESEM (Fig. 1b and S2) and TEM (Fig. 1c) images reveal a sheet-like morphology for the as-obtained BiOBr. The HRTEM images of the S-BiOBr-2 NSs exhibit a distinct lattice fringe spacing of 0.283 nm (Fig. 1d), which corresponds to the

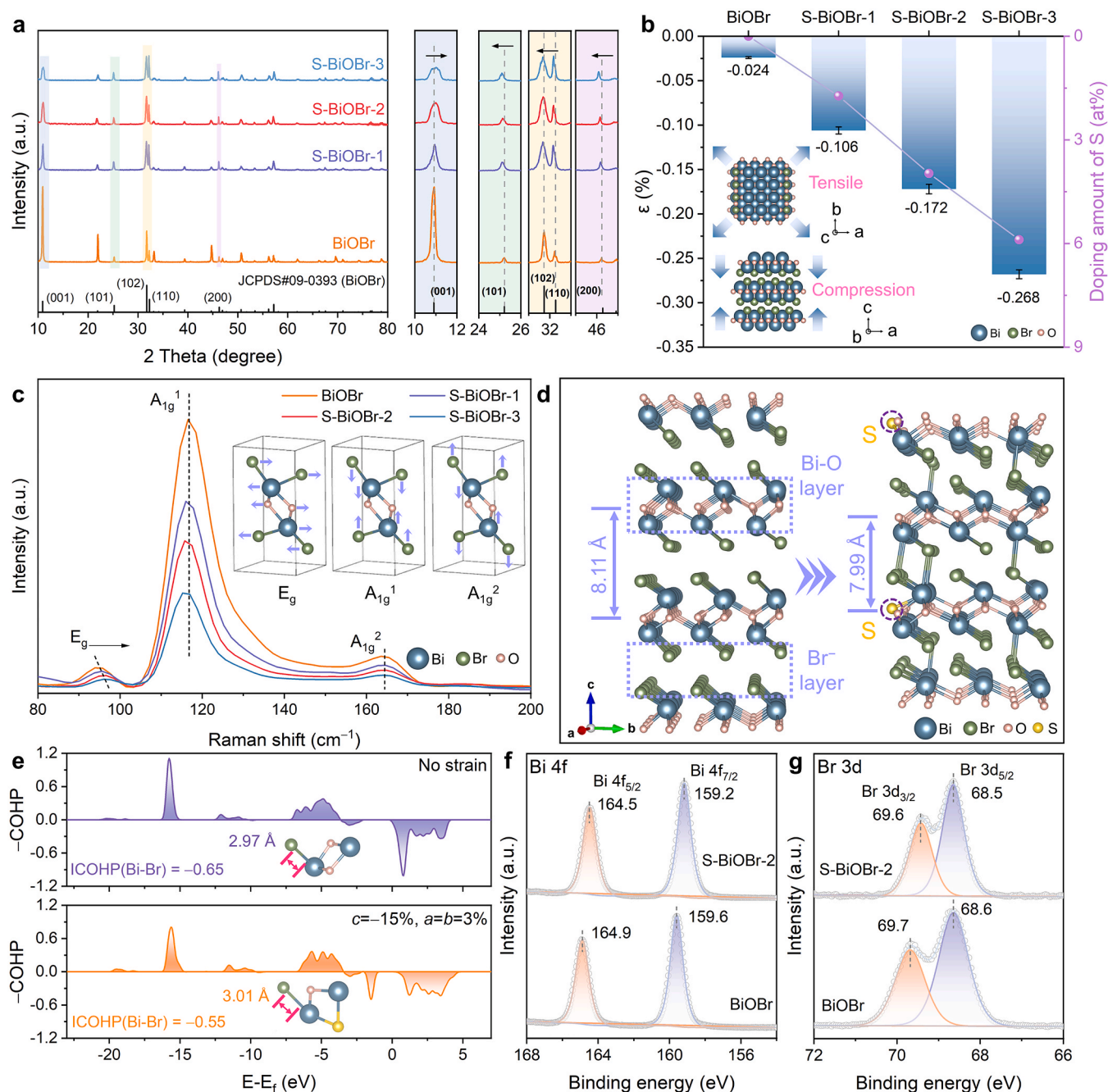


Fig. 2. (a) XRD patterns and (b) average strain values of BiOBr and comparison samples. (c) Raman spectra of the as-prepared catalysts. (d) Optimized ball-stick model for BiOBr and S-BiOBr. (e) COHP plots of BiOBr and S-BiOBr, where the Bi–Br bonding interactions are quantified by the COHP (i.e., the product of the Hamiltonian matrix elements and the density-of-states matrix). High-resolution XPS spectra of (f) Bi 4f, and (g) Br 3d for BiOBr and S-BiOBr-2.

(102) plane of BiOBr. The SAED pattern of S-BiOBr-2 NSs (inset, Fig. 1e) shows irregular diffraction rings corresponding to the (101), (102), (111), and (200) crystal planes. The reciprocal spacing, relative intensity, and intensity-spacing profile are summarized in Fig. 1e, all major diffraction signals are assignable to phase-pure S-BiOBr-2 with no impurities detected, indicating preferential crystal orientation. Additionally, energy dispersive spectroscopy (EDS) elemental mapping of S-BiOBr-2 reveals a homogeneous distribution of Bi, O, Br, and S atoms (Fig. S3), suggesting that S atoms are uniformly doped into the BiOBr structure. The morphology and structure of S-BiOCl and S-BiOI are similar to those of S-BiOBr-2 (Fig. S4–S6). As elemental doping typically induces lattice distortion, we sought to confirm the distribution of tensile and compressive strain at the atomic scale. To this end, we selected a

representative S-BiOBr-2 nanocrystal and performed geometric phase analysis (GPA). Tensile strains are evidenced by colors that span from green to bright yellow, while compressive strains are represented by colors ranging from green to dark blue [28]. The E_{xx} , E_{yy} , and E_{xy} represent the strain in the horizontal direction applied to the vertical side of the lattice, the strain in the vertical direction exerted on the horizontal side of the lattice, and the shear strain acting on the lattice, respectively. As shown in Fig. 1f, the lattice of S-BiOBr-2 exhibits tensile strain in the horizontal direction and significant compressive strain in the vertical direction, with negligible tangential strain. In contrast, no distinct strain is observed in the lattice of pristine BiOBr (Fig. 1g), indicating that the observed lattice distortion originates from S doping. In addition, AFM analysis reveals that the thickness of the S-BiOBr-2 NSs

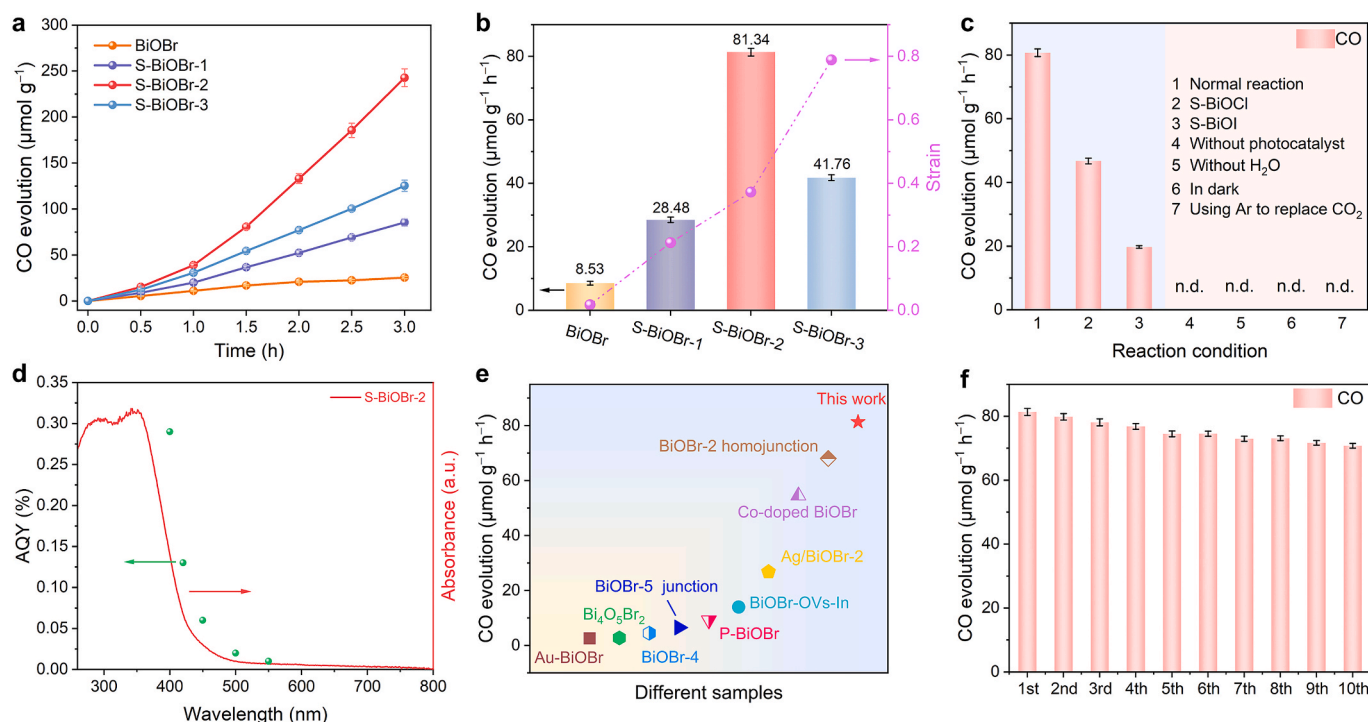


Fig. 3. (a) Time-resolved gas evolution profiles and (b) average CO evolution rates for different samples. (c) Control experiments for PCR performances under various conditions, where n.d. denotes not detected. (d) AQY of S-BiOBr-2 for PCR under monochromatic light illumination ($\lambda = 400, 420, 450, 500, \text{ and } 550 \text{ nm}$) in reference to its UV-vis DSR. (e) Comparison of CO evolution rates over BiOBr in this work and previously reported systems. (f) Cyclic tests of S-BiOBr-2.

(3.50 nm) is nearly identical to that of pristine BiOBr (3.53 nm) (Fig. S7), suggesting that S doping only induces localized lattice distortion without affecting the sheet-shaped morphology.

The XRD patterns of the synthesized S-BiOBr and comparative samples are shown in Fig. 2a. All XRD patterns indicate a tetragonal structure of BiOBr (JCPDS card #09-0393) without the formation of any new crystalline phases. Particularly, the (0 0 1) diffraction peak exhibits an obvious high-angle shift, which corresponds to the compressive strain along the [0 0 1] direction, resulting in a reduction in the lattice spacing of the (001) plane [29]. Notably, the reduction in the diffraction intensity of the (001) peak with increasing S content was attributed to the lattice distortion resulting from the incorporation of S, which preferentially diminished the structural order along the [001] direction. The (101), (110), and (200) diffraction peaks of S-BiOBr gradually shift towards lower angles, indicating a progressive increase in the corresponding planar spacings. Such a pronounced changes in lattice spacing are attributed to S-doping-induced microscopic lattice distortion [30]. Table S1 summarizes the lattice constants for all synthesized materials, which were extracted via full-pattern fitting of their respective XRD data. With the increasing amount of S doping, the lattice constants a and b exhibit a gradual expansion, whereas the c -axis undergoes a continuous contraction. This phenomenon indicates the existence of tensile strain within the lattice throughout the ab -plane, whereas compression occurs along the c -axis (inset, Fig. 2b), which is also in line with the GPA analysis. Although substituting the smaller O atoms with larger S atoms expands the in-plane lattice (a and b axes), it simultaneously triggers a contraction along the out-of-plane direction (i.e., the c -axis) driven by the Poisson effect typical of 2D layered materials [31]. This geometric compensation minimizes the total elastic strain energy, effectively accounting for the macroscopic c -axis compression and reduced interlayer spacing. Furthermore, an elemental analyzer was employed to determine the sulfur content in the S-doped samples (Table S2). Subsequently, the specific distortion was evaluated by the crystal microstrain curve (Fig. S8) derived from the Williamson–Hall Equation S12 [32,33]. The average compressive stress (ϵ) shows a progressive increase in

magnitude from -0.024% for BiOBr to -0.268% for S-BiOBr-3 (Fig. 2b), confirming that the compressive strain originates from S doping. The Raman spectra in Fig. 2c show three typical vibrational signals at 92, 114, and 162 cm^{-1} corresponding to the E_g (the vibrations of the constituent atoms across the ab -plane), A_{1g} , and A_{2g} (symmetrical stretching vibration of the Bi–O bond along different crystallographic directions) modes of BiOBr, respectively [34]. Significantly, with increasing S doping, the Raman peaks of the E_g mode shift towards higher wave-numbers, implying a progressive change in the structural symmetry, which is concomitant with the gradual stretching of the ab -plane [29]. The slight blue shift of A_{1g} peak is ascribed to the shortening of the c -axis (a reduction in the layer spacing) induced by S doping, as well as the strengthened interaction between the interlayer Br atoms and adjacent $[\text{Bi}_2\text{O}_2]^{2+}$ layers. Conversely, the decreased intensity of the A_{1g} and A_{2g} peaks can be attributed to the weakened Bi–O bonds resulting from S atom substitution for O [35,36]. Additionally, based on the previously reported work [37], the interlayer spacing was determined by extracting the vertical distances between the intermediate O atoms in adjacent $[\text{Bi}_2\text{O}_2]$ layers from the optimized DFT model along the c -axis. The calculation demonstrated a decrease from $8.11 \text{ \AA}$ in pristine BiOBr to $7.99 \text{ \AA}$ upon S doping, further validating that S doping compresses BiOBr along the [001] direction (c -axis) (Fig. 2d and Fig. S9). The absolute value of the integrated crystal orbital Hamiltonian projection (ICOHP) for the S-doped Bi site and neighboring Br decreases with increasing strain (Fig. 2e), indicating weakened Bi–Br bonding strength with values of -0.55 and -0.65 for the S-BiOBr and BiOBr samples, respectively. This reduction results from compression-induced changes in the Bi coordination environment, which modify the electronic distribution around Bi and weaken the Bi–Br interaction [38]. XPS was employed to analyze the chemical states and composition of BiOBr and S-BiOBr-2 (Fig. S10). The S 2p XPS spectra of S-BiOBr-2 (Fig. S11a) confirmed the presence of S doping. The Bi 4f spectra (Fig. 2f) at 159.6 eV and 164.9 eV were indexed to Bi $4f_{7/2}$ and Bi $4f_{5/2}$ of BiOBr, respectively. Compared with BiOBr, the Bi 4f binding energy of S-BiOBr-2 slightly shifted to a lower energy level, indicating increased electron density at Bi sites due

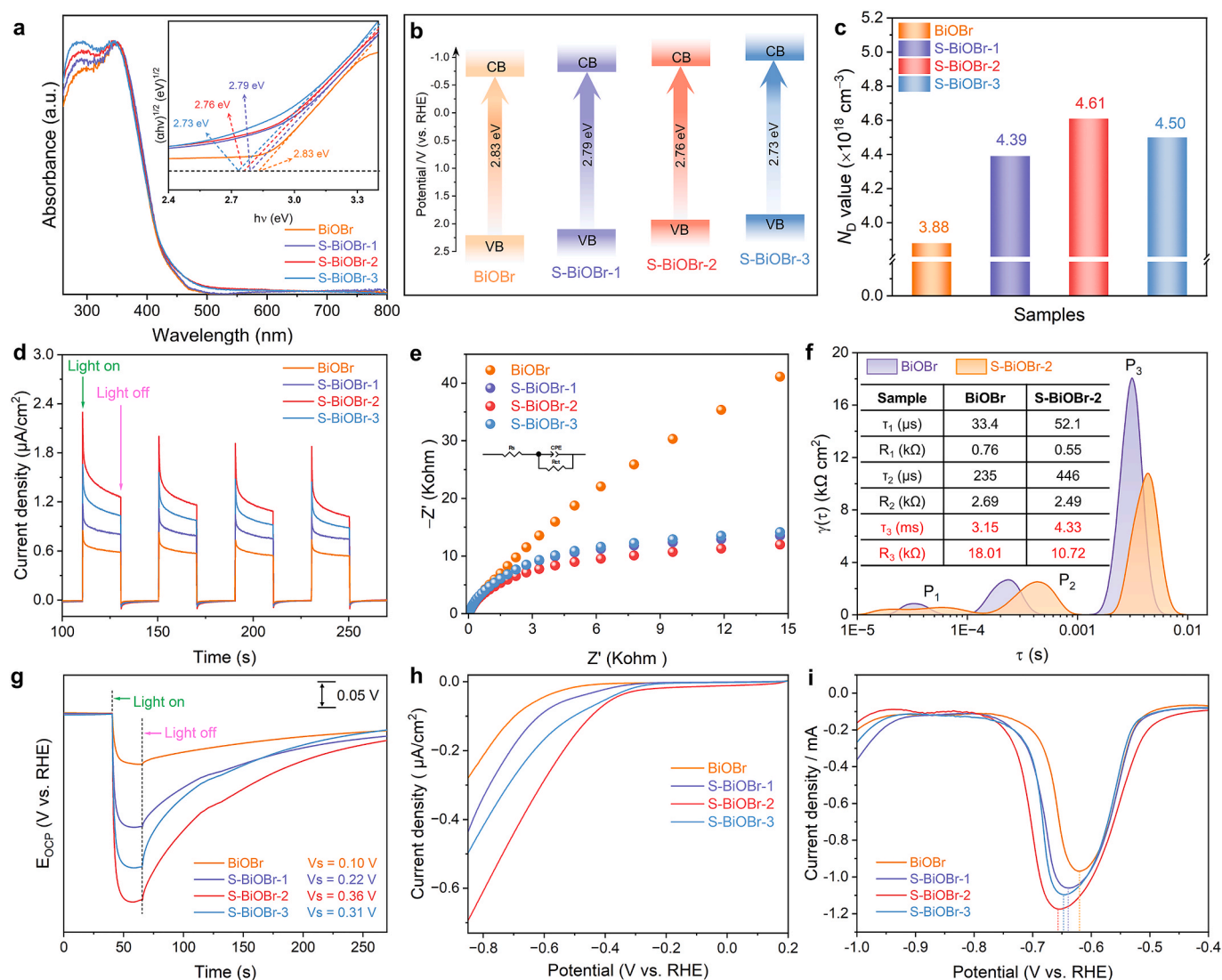


Fig. 4. (a) UV-Vis DRS (inset: Tauc plot) and (b) band alignment of the as-prepared samples. (c) Donor density from $M - S$ plots. (d) Transient photocurrent and (e) EIS spectra of S-BiOBr-2 and contrast samples. (f) DRT analysis of EIS for BiOBr and S-BiOBr-2. (g) Time-dependent E_{OCP} plots, (h) LSV, and (i) DPV-driven redox potentials for S-BiOBr-2 and contrast samples.

to electron donation from S ($\chi_p = 2.58$) replacing O ($\chi_p = 3.44$) [39]. Similarly, the Br 3d peaks shifted slightly to lower binding energies from 69.7 and 68.6 eV for BiOBr to 69.6 and 68.5 eV for S-BiOBr-2 (Fig. 2g), which corroborates the direction of electron migration previously proposed. In the O 1s spectra of BiOBr (Fig. S11b), three peaks at 530.2, 531.8, and 533.1 eV were categorized as lattice oxygen, surface hydroxyl, and adsorbed water, respectively [29]. The shifted lattice oxygen peak in S-BiOBr-2 suggests an altered electron density around oxygen, resulting from lattice distortion induced by S substitution at O sites [40]. XES was performed at the Bi $M\alpha$ -edges to further understand the electrical structure (Fig. S12). In comparison to pristine BiOBr, the main emission peak of S-BiOBr-2 exhibits a slight shift (~ 0.16 eV) towards lower energies (as indicated by the dashed lines in Fig. S12b). Although the overall spectral profiles remain mostly unchanged, this subtle low-energy shift reflects a minor modulation of the local electron density around the Bi atoms. This arises from the substitution of O with the less electronegative sulfur, which is consistent with the electron enrichment and the lowered Bi 4f binding energy observed in XPS results. The results mentioned above suggest that S doping leads to a decrease in the interlayer spacing and modulates the chemical environment at the Bi site, both of which provide favorable conditions for promoting CO_2

adsorption and activation.

3.2. Evaluation of photocatalytic performance

The photocatalytic CO evolution efficiency of BiOBr and S-doped BiOBr samples, evaluated in a gas-solid reaction system using water as proton donor without other sacrificial agents or photosensitizers, increases linearly with illumination time (Fig. 3a). No other gaseous reduction products (such as H_2 or CH_4) were detected. Fig. 3b displays the average CO generated after 3 h reaction. The pristine BiOBr exhibits a CO generation rate of $8.53 \mu\text{mol g}^{-1} \text{ h}^{-1}$. With the gradual increase in the amount of S doping, the performance of the S-doped BiOBr samples were improved under the influence of the generated lattice strain. Among them, the S-BiOBr-2 exhibits the highest CO evolution rate ($81.34 \mu\text{mol g}^{-1} \text{ h}^{-1}$), which is approximately 9.53 times that of pristine BiOBr and surpasses most reported BiOBr-based catalysts (Table S3). This enhancement originates from the improved interlayer charge separation and migration efficiency, driven by the compressive strain induced by S doping. However, the decline in PCR performance when the S content is further increased ($41.76 \mu\text{mol g}^{-1} \text{ h}^{-1}$ for S-BiOBr-3) may be attributed to excessive strain and generation of a high density of

defects, which disrupt the long-range structural order of the lattice. The positive effects of reduced interlayer spacing are eventually negated by substantial lattice disorder, which also hinders the creation of continuous and effective routes for interlayer charge transport [41]. O_2 derived from water is widely recognized as the oxidation product in PCR reactions without sacrificial reagents. Therefore, the generated O_2 was further characterized. As shown in Fig. S13, the O_2 yield correlates strongly with the formation rate of CO product, indicating that S-doping-induced strain engineering effectively enhances overall photocatalytic efficiency. Isotopic labeling experiments using $^{13}CO_2$ instead of $^{12}CO_2$ yielded a clear signal at $m/z = 29$ (Fig. S14), confirming that the produced CO stems from CO_2 reduction. To rigorously verify the origin of the CO products, a series of controlled experiments were performed (Fig. 3c). No CO was detected in the absence of either light irradiation or the photocatalyst, confirming that CO production is strictly photocatalytic and catalyst-dependent. When the CO_2 feed was replaced with Ar, no carbon-containing reduction products were observed, confirming that the evolved CO originates exclusively from the supplied CO_2 . Moreover, complete omission of H_2O completely suppressed CO evolution, unambiguously establishing H_2O as the sole proton source essential for this reduction pathway. Additionally, we conducted control experiments using pure thiourea and a physical mixture of pristine BiOBr with thiourea at a loading corresponding to the sulfur content (1.29 wt%) of S-BiOBr-2. As illustrated in Fig. S15, pure thiourea exhibited negligible CO evolution rate of $1.44 \mu mol g^{-1} h^{-1}$, likely due to its decomposition under illumination. The BiOBr/thiourea physical mixture also showed negligible activity ($10.48 \mu mol g^{-1} h^{-1}$) under identical conditions, confirming that physical mixing cannot replicate the enhancement achieved by sulfur doping. Thus, the enhanced CO evolution on S-BiOBr-2 is unequivocally attributable to the sulfur doping effect, rather than to any interference from extraneous sulfur species. The compressive strain strategies can be extended to other members of the BiOX family (BiOCl and BiOI). Notably, the CO evolution rates of S-BiOCl and S-BiOI are 46.7 and $19.7 \mu mol g^{-1} h^{-1}$, respectively, higher than those of their pristine counterpart ($5.32 \mu mol g^{-1} h^{-1}$ for BiOCl and $2.87 \mu mol g^{-1} h^{-1}$ for BiOI) under identical test conditions (Fig. S16). The enhancement factors induced by S doping for S-BiOCl, S-BiOBr-2, and S-BiOI were calculated to be 8.77, 9.53, and 6.87-fold for BiOCl, BiOBr, and BiOI, respectively. This performance trend, wherein BiOBr exhibited superior performance compared to BiOCl and BiOI, suggests that the regulatory mechanism of stress engineering on PCR performance is also intricately associated with the inherent properties of the catalyst. Compared to BiOBr, BiOI has a larger interlayer spacing and weaker bonding, which can induce structural instability under compressive strain and negate its inherent advantages. Conversely, BiOCl's smaller initial spacing and stronger interlayer interactions likely make it less susceptible to strain-induced modification. This assessment is corroborated by the crystal microstrain analysis derived from the Williamson-Hall Equation S12 and Fig. S17. BiOBr attains the optimal balance by most effectively accommodating strain to boost charge dynamics while maintaining stability, thereby achieving excellent performance. The apparent quantum yield (AQY) was also measured to evaluate the photon conversion efficiency (Eqs. (1) and (2)). Under band-pass filter irradiation at 400, 420, 450, 500, and 550 nm, the AQY values for S-BiOBr-2 reached 0.29%, 0.13%, 0.063%, 0.021%, and 0.0097%, respectively (Fig. 3d and S1), and are comparable to those of previously reported BiOBr-based photocatalysts (Fig. 3e and Table S3). As shown in Fig. 3f and Fig. S18, the CO evolution rates of S-BiOCl, S-BiOBr-2, and S-BiOI after ten cycles decreased by only 14.9%, 13.1%, and 18.7%, respectively, relative to their initial rates. In addition, S-BiOBr-2 exhibits excellent stability during the 20 h continuous CO evolution experiment (Fig. S19), achieving a total CO yield of $1855.3 \mu mol g^{-1}$. Furthermore, no noticeable structural changes were detected in the XRD patterns (Fig. S20a) or SEM images (Fig. S21) after the cyclic tests, and the chemical states of Bi, Br, O, and S in S-BiOBr-2 remained unchanged as confirmed by XPS analysis (Fig. S20). These results collectively confirm

that S-BiOBr-2 possesses robust structural stability, capable of accommodating the doping-induced compressive strain without suffering long-term lattice degradation.

3.3. Band structure and carrier separation kinetics

To reveal the underlying mechanism for the excellent photoreduction properties of the S-doped BiOBr samples, the light response and energy band structure of the S-BiOBr catalyst were investigated by UV-Vis DRS and M-S curves [42]. As shown in Fig. 4a, S doping enhances light absorption and reduces the bandgap (E_g), as derived from Tauc plots. M-S curves were utilized to obtain the flat-band potentials (E_{fb}) of BiOBr and S-BiOBr (Fig. S22), and then the conduction band (CB) position was estimated by M-S curves based on the n-type semiconductor characteristics [43]. Consequently, the estimated CB values are -0.61 , -0.70 , -0.81 , and -0.89 V (vs. RHE), respectively. Combined with the E_g , the band structures of BiOBr and S-BiOBr were further derived (Fig. 4b). This strain-tuned band structure optimizes both light absorption and electron reduction ability, thereby enhancing CO_2 reduction. To further evaluate how the S-doping-induced reduction in interlayer spacing affects charge separation and transfer, we assessed the resulting impedance to carrier migration. This was quantitatively verified by evaluating the carrier density (N_D) for the different catalysts from M-S analysis (Fig. S22 and S23) [44,45], using the following formula (Eq. (3)):

$$N_D = \frac{2}{\epsilon \epsilon_0 e} \frac{dV}{d\frac{1}{C_2}} = \frac{2}{\epsilon \epsilon_0 e} \frac{1}{\text{slope}} \quad (3)$$

where ϵ is the dielectric constant of the semiconductor (21.62 for BiOBr) [46], ϵ_0 is the vacuum dielectric constant (8.85×10^{-14} F cm $^{-2}$), and e is the electron charge (1.6×10^{-19} C). The N_D values of the BiOBr, S-BiOBr-1, S-BiOBr-2, and S-BiOBr-3 samples were calculated to be 3.88×10^{18} , 4.50×10^{18} , 4.61×10^{18} , and 4.39×10^{18} cm $^{-3}$ (Fig. 4c). To quantitatively evaluate the strength of the built-in electric field (BIEF) arising from doping-induced lattice strain, the surface electric field intensity (F_s), a direct measure of the BIEF, was calculated using Kanata's model [47]. The detailed calculation parameters and corresponding results are presented in Fig. S24 (Supplementary Information). As shown in Fig. S25, the normalized F_s for S-BiOBr-2 exhibits a 4.69-fold increase compared to that of pristine BiOBr (defined as 1.00), confirming that an optimized level of interlayer compressive strain can significantly reinforce the BIEF, thereby providing a robust internal driving force to promote spatial charge separation. We further investigated the effect of S doping on the photoelectric properties of the catalysts. Steady-state PL spectra (Fig. S26) show quenched emission for S-BiOBr-2, indicating suppressed charge recombination. Consistently, the S-BiOBr-2 exhibits a higher photocurrent (Fig. 4d) and lower EIS signals (Fig. 4e), confirming improved charge separation and transfer, consistent with the calculated N_D . The EIS time-domain data were further analyzed using the distribution of relaxation times (DRT) to resolve the different resistance components [48]. Fig. 4f shows that while mass transfer resistance (diffusion resistance in the catalyst surface or bulk phase, R_1 and R_2) remains similar between BiOBr and S-BiOBr-2 [49], the charge transfer resistance (resistance to electron transfer from the catalyst surface to CO_2 molecules/intermediates, R_3) for S-BiOBr-2 is nearly halved. This result indicates that S doping leads to a reduction in interlayer spacing, enhancing interlayer electron migration and charge transfer kinetics without disrupting the overall layered framework, and the doping sites do not affect the mass transport path. Furthermore, S-BiOBr-2 demonstrates a more positive OCP (Fig. 4g) and lower overpotential at equal current density (Fig. 4h), confirming enhanced reaction kinetics [50]. DPV results (Fig. 4i) show enhanced electron reduction ability after S doping, attributable to the negative shift of the Fermi level [51]. In summary, S doping reduces the interlayer spacing, speeds up charge separation and transfer, and optimizes carrier kinetics.

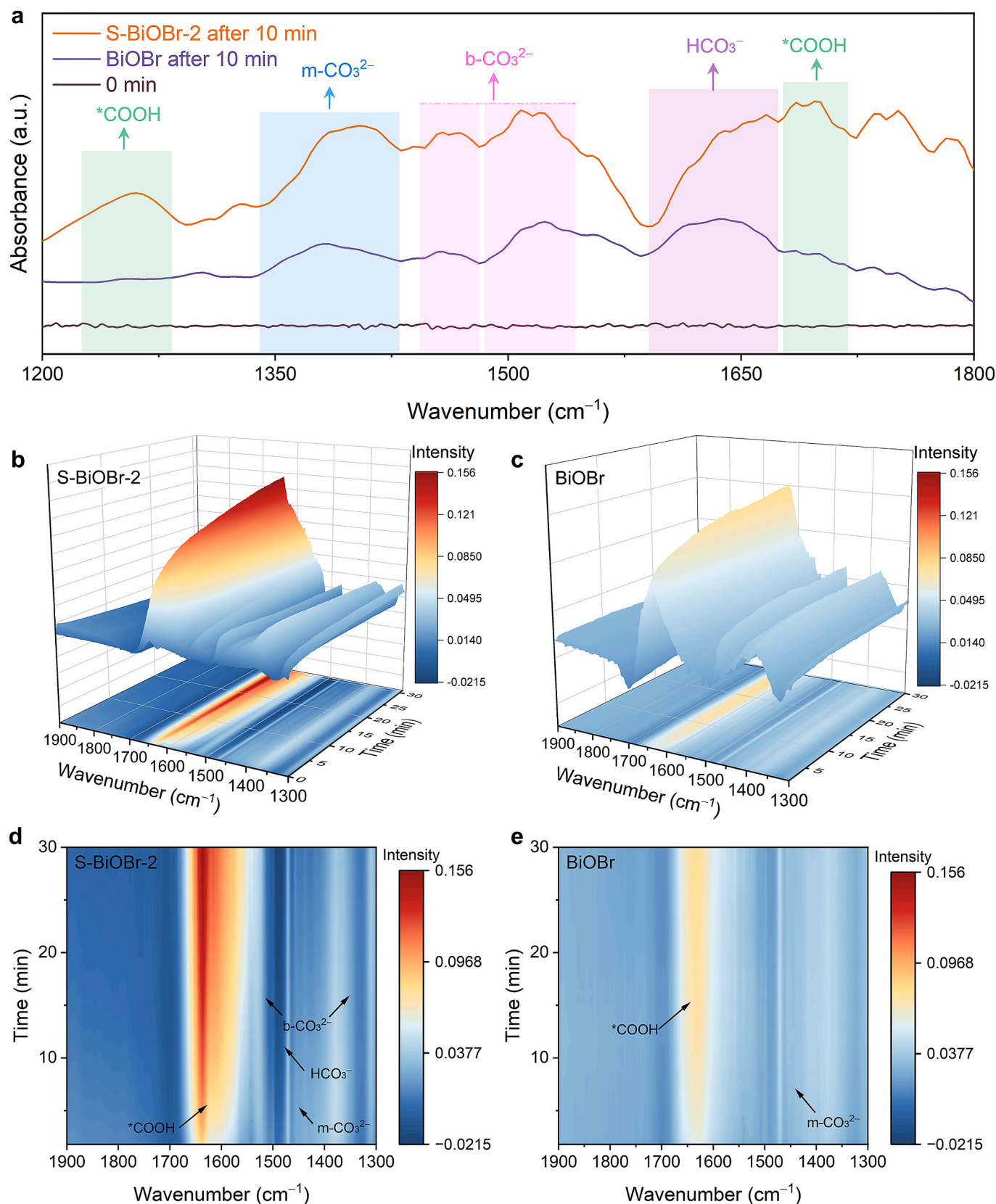


Fig. 5. (a) In-situ DRIFTS spectra of CO₂ adsorbed on S-BiOBr-2 and BiOBr after 10 min in the dark. (b) 3D surface plot of in-situ DRIFTS spectra for S-BiOBr-2 and (c) for BiOBr; (d) and (e) are the corresponding contour maps, respectively. The in-situ DRIFTS measurements were performed on the as-prepared samples exposed to a flowing mixture of Ar, CO₂, and H₂O vapor, both in the dark and under irradiation.

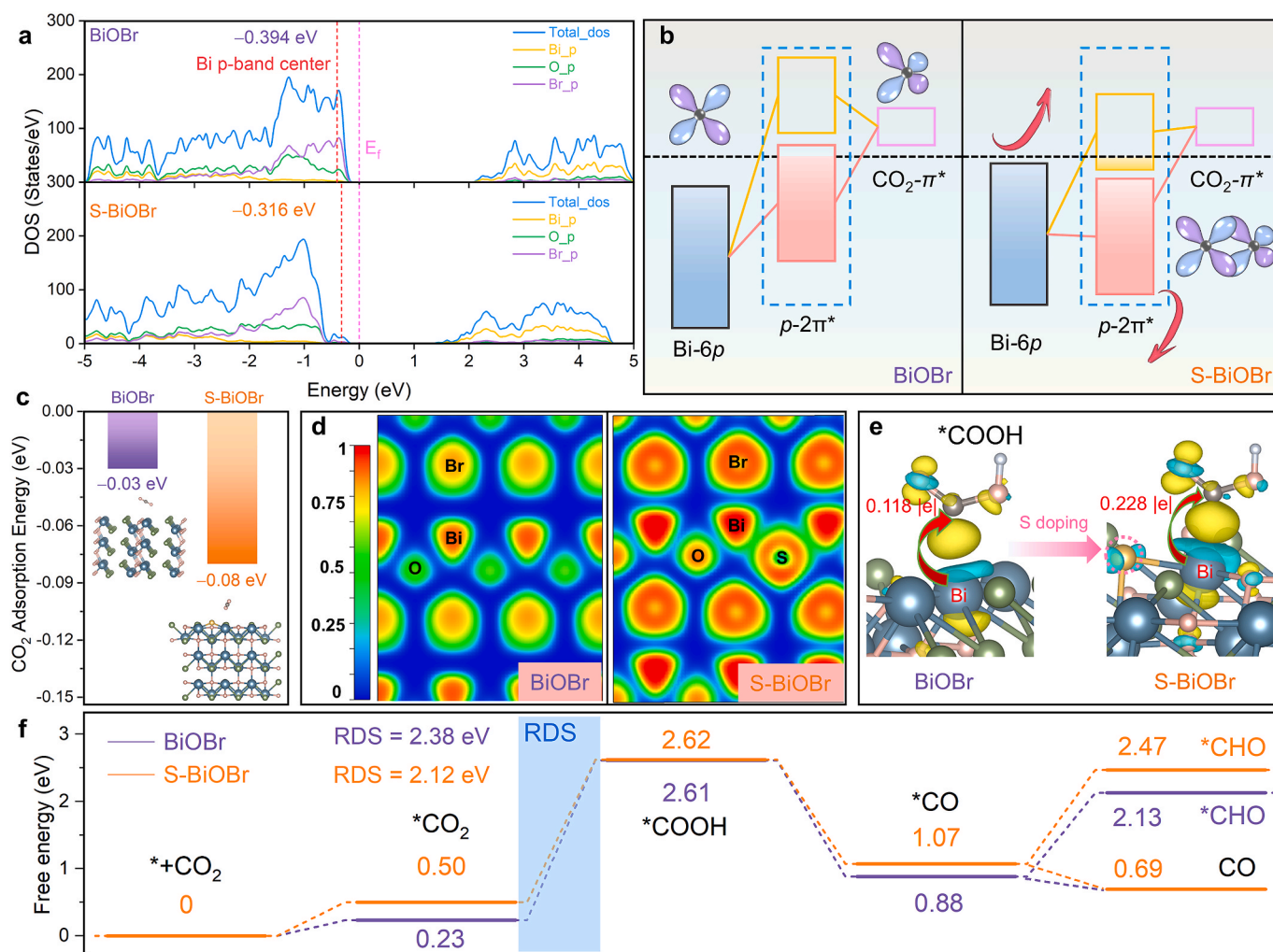


Fig. 6. (a) Calculated DOS of BiOBr and S-BiOBr (red and pink dashed lines represent the p-band centers and E_f , respectively). (b) Illustration of how 6p-2 π^* spin-down DOS affects CO₂ adsorption strength. (c) Calculated CO₂ adsorption energies at Bi active centers of BiOBr and S-BiOBr. (d) Electron localization function of BiOBr and S-BiOBr. (e) Charge densities differences of BiOBr and S-BiOBr upon $^*\text{COOH}$ adsorption at the Bi site, with the corresponding ball-and-stick model of the intermediates (Bi, Br, O, S, and C atoms are represented by grayish blue, grayish green, coral pink, light yellow, and grayish brown colors, respectively). (f) Gibbs free energy diagrams for CO₂ reduction on BiOBr and S-BiOBr. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

3.4. Theoretical investigations of PCR mechanism

To further investigate the catalytic mechanism of S-BiOBr in PCR, the activation and reduction of adsorbed CO₂ ($^*\text{CO}_2$) were first analyzed by In-situ DRIFTS (Fig. 5 and S27). Dark adsorption experiments revealed that the S-BiOBr-2 exhibited stronger IR absorption peaks than pristine BiOBr in the 1200 ~ 1800 cm⁻¹ region (Fig. 5a), suggesting enhanced adsorption and stabilization of CO₂ and carbonates/bicarbonates intermediates. This enhanced adsorption was further confirmed by the higher CO₂ desorption peak intensities observed in CO₂-TPD measurements (Fig. S28). Furthermore, this enhanced gas-solid affinity is also reflected by a significantly increased N₂ adsorption (Fig. S29). These results collectively confirm that the S-BiOBr-2 surface exhibits enhanced CO₂ adsorption and activation capabilities, thereby establishing the prerequisite for subsequent accelerated reduction reactions. Subsequently, with the introduction of light, key intermediates were detected over S-BiOBr-2, including monodentate carbonate (m-CO_3^{2-} , 1298 cm⁻¹), bidentate carbonate (b-CO_3^{2-} , 1370 and 1627 cm⁻¹), and bicarbonate (HCO_3^- , 1650 cm⁻¹) (Fig. 5b,d and S27a) [52–54]. In contrast, the pristine BiOBr exhibited only minimal spectral changes, with m-CO_3^{2-} being the sole carbonate species observed (Fig. 5c,e and S27b). This stark difference confirms that S doping alters the electronic

structures of BiOBr, creating conditions that favor the formation of the energetically more stable b-CO_3^{2-} and leading to enhanced CO₂ reduction activity [55]. More importantly, additional peaks appeared at 1616 cm⁻¹, characteristic of the asymmetric stretching vibrations of the $^*\text{COOH}$ intermediate [56]. The presence of $^*\text{COOH}$, the key rate-determining species in the CO₂-to-CO conversion pathway, provides direct experimental evidence for the proton-coupled electron transfer step from CO₂ to $^*\text{COOH}$. Notably, the $^*\text{COOH}$ peak intensity on S-BiOBr-2 shows a more pronounced increase with prolonged illumination time than that on pristine BiOBr, indicating that S doping facilitates the formation and accumulation of this crucial intermediate, thereby accelerating the overall reaction kinetics. The improved performance is attributed to the combined effects of stronger CO₂ adsorption capacity and enhanced charge transfer, the latter resulting from the reduced interlayer spacing. Based on the evidence, the most likely reaction pathways for PCR are shown in Equations S1–S5.

DFT calculations were performed on BiOBr and S-BiOBr to elucidate the mechanism behind the enhanced PCR performance of the S-BiOBr. As shown in Fig. 6a, the density of states (DOS) and corresponding p-band centers were calculated to identify active sites and their interactions with intermediates [57]. Notably, S doping reduces the bandgap of BiOBr, consistent with Tauc plot analysis. Additionally, the

upward shift of the Bi p-band center in S-BiOBr (-0.316 eV) compared to BiOBr (-0.394 eV) confirms electron transfer from S to adjacent Bi, increasing electron density around Bi and correspondingly shifting its p-band center upward [58]. As illustrated in the schematic (Fig. 6b and S30), the raised energy level of the unoccupied Bi orbital reduces the energy level difference with the CO₂ LUMO (the π^* anti-bonding orbital), resulting in lower electron occupancy in anti-bonding states and thereby strengthening chemisorption and promoting electron transfer from catalyst to CO₂ [59]. This enhanced adsorption is clearly supported by the higher CO₂ adsorption energy on S-BiOBr (-0.08 eV) than on BiOBr (-0.03 eV) in Fig. 6c, which is consistent with the CO₂-TPD results. To verify facilitated electron transfer, electron localization function (ELF) analysis (Fig. 6d) reveals that in BiOBr, electrons are localized on Bi and Br atoms and delocalized around O atoms, with Bi serving as the primary reduction site exhibiting stronger localization. The more concentrated electron cloud around Bi reduces orbital overlap in the Bi-Br bond and weakens covalency, consistent with decreased |ICOHP|. After S doping, stronger electron aggregation around Bi sites is observed. Concurrently, the calculated work function (Φ) decreases from 5.761 eV (BiOBr) to 5.630 eV (S-BiOBr) as shown in Fig. S31, confirming the upward shift of the Fermi level and the lowered barrier for surface electron emission. This reduced work function is fully consistent with the enhanced BIEF, which synergistically boosts the interfacial charge transfer kinetics. Charge density difference calculations of *COOH adsorption (Fig. 6e) show that Bader charge transfer between *COOH and S-BiOBr (0.228 |e|) exceeds that with BiOBr (0.118 |e|), indicating greater electron injection from Bi sites into C=O anti-bonding orbitals of the carboxyl intermediate [60]. This enhanced electron donation strengthens the interaction between *COOH and the S-BiOBr surface, as evidenced by a more bent *COOH adsorption geometry (Fig. S32, 125.6° vs. 128.4°), which facilitates the subsequent C–O bond cleavage toward CO formation. Finally, the reaction pathways for CO₂ reduction were explored by calculating the Gibbs free energies of BiOBr and S-BiOBr (equations S6–S10, Fig. S33 and S34). The profiles (Fig. 6f) confirm that the rate-determining step (RDS) is *COOH formation, with S-BiOBr reducing the energy barrier from 2.38 eV to 2.12 eV, aligning with band hybridization facilitating *COOH generation. Furthermore, evaluation of the competitive deep reduction pathway reveals that protonation of *CO to *CHO involves substantial uphill energy barriers of 1.40 eV (from 1.07 to 2.47 eV) for S-BiOBr and 1.25 eV (from 0.88 to 2.13 eV) for pristine BiOBr. These barriers are significantly higher than that for direct CO desorption, effectively suppressing deep hydrogenation and thereby elucidating the experimentally observed high CO selectivity.

4. Conclusions

In summary, this study presents a doping-driven lattice strain strategy to synergistically enhance interlayer charge transport and CO₂ activation in layered photocatalysts. Using BiOX as a model system, S-doping introduces compressive strain that compresses the interlayer spacing, effectively shortening the (001) interlayer distance. This structural modification provides a rapid vertical electron channel, significantly enhancing charge separation efficiency and suppressing bulk recombination. Meanwhile, the strain optimizes the electronic structure of Bi sites, causing an upward shift of the p-band center and increasing the electron density to strengthen the orbital hybridization of CO₂. The synergistic charge dynamics and reactant activation lower the formation barrier of the *COOH intermediate, guiding the kinetics toward efficient CO production. The optimal S-BiOBr-2 NSs exhibit a CO evolution rate of $81.34 \mu\text{mol g}^{-1} \text{h}^{-1}$, which is 9.53 times higher than that of pristine BiOBr and exceeds that of S-BiOCl ($46.7 \mu\text{mol g}^{-1} \text{h}^{-1}$) and S-BiOI ($19.7 \mu\text{mol g}^{-1} \text{h}^{-1}$). This work provides profound atomic-level insight into how strain engineering simultaneously regulates charge dynamics and surface catalysis, establishing a versatile paradigm for the design of high-performance layered photocatalysts.

CRediT authorship contribution statement

Kangjie Gao: Writing – original draft, Validation, Data curation, Conceptualization. **Yuanyuan Zhao:** Validation, Formal analysis, Data curation, Conceptualization. **Huanhuan Liu:** Writing – original draft, Funding acquisition, Data curation, Conceptualization. **Jiaxin Li:** Formal analysis, Data curation. **Peisen Luo:** Validation, Formal analysis. **Fang Chen:** Validation, Software, Data curation, Conceptualization. **Wentao Wang:** Visualization, Validation, Software, Methodology. **Yong Hu:** Writing – review & editing, Supervision, Project administration, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jcat.2026.117194>.

Data availability

The authors do not have permission to share data.

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