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Isolated single atom cobalt in $\text{Bi}_3\text{O}_4\text{Br}$ atomic layers to trigger efficient CO_2 photoreduction

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The design of efficient and stable photocatalysts for robust CO_2 reduction without sacrifice reagent or extra photosensitizer is still challenging. Herein, a single-atom catalyst of isolated single atom cobalt incorporated into $\text{Bi}_3\text{O}_4\text{Br}$ atomic layers is successfully prepared. The cobalt single atoms in the $\text{Bi}_3\text{O}_4\text{Br}$ favors the charge transition, carrier separation, CO_2 adsorption and activation. It can lower the CO_2 activation energy barrier through stabilizing the COOH^* intermediates and tune the rate-limiting step from the formation of adsorbed intermediate COOH^* to be CO^* desorption. Taking advantage of cobalt single atoms and two-dimensional ultrathin $\text{Bi}_3\text{O}_4\text{Br}$ atomic layers, the optimized catalyst can perform light-driven CO_2 reduction with a selective CO formation rate of $107.1 \mu\text{mol g}^{-1} \text{h}^{-1}$, roughly 4 and 32 times higher than that of atomic layer $\text{Bi}_3\text{O}_4\text{Br}$ and bulk $\text{Bi}_3\text{O}_4\text{Br}$, respectively.

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Photocatalytic CO₂ reduction with water as reaction medium to yield value-added carbon products has been regarded as an appealing approach to remit the energy issue and manage the global carbon balance simultaneously^{1–5}. Despite a good deal of impressive photocatalysts have been developed for CO₂ reduction, most of them are still subjected to low photocatalytic activity, poor product selectivity or the requirement of sacrificial agent, which greatly limit the possible practical applications. Hence, it is desirable to design robust catalysts with high reduction efficiency, high selectivity without the utilization of sacrifice reagent.

Recently, ultrathin two-dimensional (2D) materials with suitable energy band structure have been demonstrated distinct advantages as one class of emerging photocatalysts^{6–10}. The atomic thickness with concomitant huge specific surface area allows better absorption of ultraviolet-visible light. The ultrathin configuration can significantly decrease the bulk recombination possibility of charge carriers owing to the shortened diffusion distance from inside to surface. Moreover, the high ratio of coordination-unsaturated surface atoms to overall atoms can afford more sites facilitating the interfacial reactions¹¹. Especially, the single species of surface atoms is conducive to the production of highly selective CO₂ reduction products^{12–14}. Up to now, several types of ultrathin nanosheets have been developed and employed for CO₂ photoreduction, such as WO₃ layers¹², ultrathin ZnAl LDH¹³, single-unit-cell o-BiVO₄¹⁴, Bi₂WO₆ layers¹⁵, and one-unit-cell ZnIn₂S₄¹⁶. However, the high surface charge recombination rate and lack of active sites limits the sufficient utilization of charge carriers to trigger the photoreduction process. In order to further improve the CO₂ reduction efficiency, incorporating isolated single atoms into 2D ultrathin nanosheets may be an appealing strategy. With maximum atom-utilization efficiency and unique properties, single-atom catalysts (SAC) display enormous potential in different catalytic applications^{17,18}. Considering the cobalt (Co) SAC show outstanding performance toward electrocatalytic CO₂ reduction due to the unique electronic structure, it is desirable to introduce Co single atoms as active sites to build Co SA/2D materials and employed for CO₂ photoreduction^{19,20}. Moreover, this allocation affords a favorable platform to in-depth insight the structure–property relationship between doped single atoms and the corresponding photocatalytic activity. Herein, taking the ultrathin Bi₃O₄Br nanosheets as a prototype, isolated single-atom Co is incorporated into Bi₃O₄Br atomic layers to build a Co–Bi₃O₄Br catalyst and employed for CO₂ photoreduction.

Results

Characterizations of Co–Bi₃O₄Br nanosheets. X-ray diffraction (XRD) and Raman spectra suggest the successful preparation of orthorhombic Bi₃O₄Br and the Co incorporation did not destroy the crystal structure (Supplementary Fig. 1). The transmission electron microscopy (TEM) image in Supplementary Fig. 2a–c depicts a sheet-like morphology of Bi₃O₄Br with the thickness of 1.89 nm, corresponding to unit cell (*c* parameter) thickness of Bi₃O₄Br. The observed lattice spacing of 0.285 nm is corresponded to the (020) or (200) crystal plane spacing of Bi₃O₄Br, revealing the (002) facet exposure (Supplementary Fig. 2d). The TEM and atomic force microscope images of Co–Bi₃O₄Br-1 show the similar morphology and thickness with pure Bi₃O₄Br (Fig. 1a, b, Supplementary Fig. 3). To disclose the fine structure and distribution of Co, atomic resolution high-angle annular dark-field scanning TEM (HAADF-STEM) is performed. The isolated dark dots Fig. 1c, d can be unambiguously ascribed to individual Co atoms according to the Z-contrast difference between the light Co and the heavier Bi atoms²¹. The isolated Co atoms are

substituting Bi atoms in the crystal lattice. In addition, elemental mapping with subnanometer resolution (Fig. 1e, f) shows a uniform, uncorrelated spatial distribution of Co with a content of 0.8 wt%.

To further disclose the Co coordination environment, X-ray absorption near-edge structure and extended X-ray absorption fine structure (EXAFS) spectroscopy are performed. The difference in position and intensity of pre-edge peak at about 7711 eV signify that the Co atoms in the samples are of diverse environments (Fig. 2a)²². The Co K-edge absorption edge position of Co–Bi₃O₄Br-1 is located close to CoO rather than Co foil, suggesting single Co atom carries positive charge with the valence state is approach +2. The Bi L₃-edge absorption edge position of Co–Bi₃O₄Br-1 shows slight difference with that of Bi₃O₄Br, suggesting distinct local atomic structure due to Co incorporation (Fig. 2b). View from the Fourier transformed (FT) k³-weighted EXAFS spectra (Fig. 2c), Co–Bi₃O₄Br-1 materials does not emerge the peak of Co–Co bond in reference to standard Co foil and CoO, revealing the absence of Co or CoO clusters/particles. These results demonstrate that the Co species are isolated single atoms. The main peak at 1.49 Å for Co–Bi₃O₄Br-1 is corresponding to the coordination with O atoms in Bi₃O₄Br lattice²². Beyond that, the main peak at around 1.5 Å in Bi L₃-edge EXAFS spectra is assigned to the Bi–O bonds, in which the intensity of Co–Bi₃O₄Br-1 is weaker than that of Bi₃O₄Br (Fig. 2d)²³. All these result qualitatively verify their distinct local atomic arrangement of Co–Bi₃O₄Br-1 relative to the Bi₃O₄Br, also certified by the peak shifting in X-ray photoelectron spectra (XPS, Supplementary Fig. 4) and decreased zeta potentials from 29.9 mV for Bi₃O₄Br to 18.4 mV for Co–Bi₃O₄Br-1 (Supplementary Fig. 5).

Photocatalytic CO₂ reduction performances. The photocatalytic CO₂ reduction performance of the samples is examined in neutral water under simulated solar light irradiation without any sacrificial reagents or photosensitizers. As shown in Fig. 3a, the Bi₃O₄Br atomic layer displays a CO formation rate of 27.0 μmol g^{−1} h^{−1}, greatly higher than the 3.3 μmol g^{−1} h^{−1} for bulk Bi₃O₄Br (Supplementary Fig. 6), revealing the advantage of 2D ultrathin configuration. After the isolated single-atom Co is incorporated into Bi₃O₄Br atomic layers, the photocatalytic activity can be further improved. Among the diverse Co–Bi₃O₄Br materials, the Co–Bi₃O₄Br-1 displays the optimal performance. During a 20 h photocatalysis test, the total yield of CO can arrive 2142.1 μmol g^{−1}, accompanied by a trace amount of methane (~3.28 μmol g^{−1}). The average CO-generation rate of Co–Bi₃O₄Br-1 is up to 107.1 μmol g^{−1} h^{−1}, roughly 4 and 32 times higher than that of Bi₃O₄Br atomic layer and bulk Bi₃O₄Br, respectively. This value is also higher than many ultrathin materials under the same testing conditions (Supplementary Fig. 7) and superior to many reported results (Supplementary Table 1). During the photoreduction process, Co–Bi₃O₄Br-1 sample can simultaneously achieve H₂O oxidation into O₂ with an average O₂ evolution rates of about 56 μmol g^{−1} h^{−1} (Supplementary Fig. 8). The ratio of CO evolution rates to O₂ evolution rates is 1.91, approach to the stoichiometric ratio of 2. Through tune the different usage amount of photocatalyst for CO₂ reduction, the higher converted value of μmol g^{−1} h^{−1} can be achieved when less usage amount is employed (Supplementary Fig. 9). The control experiments in dark, under Ar condition or without catalyst did not show the evolution of CO, implying the CO is indeed produced by CO₂ photoreduction. The ¹³CO₂ isotopic labeling experiment is performed, in which the peak at *m/z* = 29 (¹³CO) can be observed, further affirming the formation of CO is indeed derived from the reduction of CO₂ (Fig. 3b). Furthermore, the apparent quantum yields for Co–Bi₃O₄Br-1 are calculated

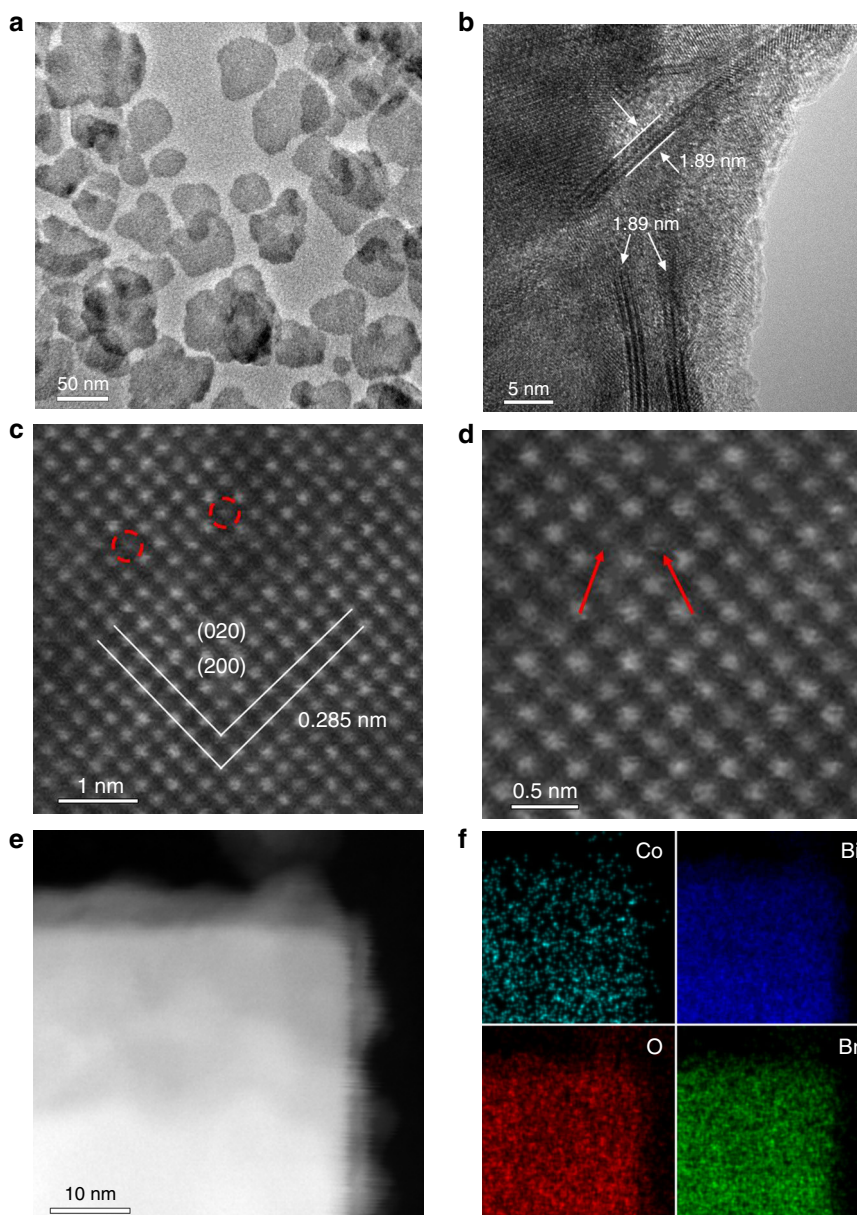


Fig. 1 Surface morphology of Co-Bi₃O₄Br-1. **a, b** TEM and **c, d** atomic resolution HAADF-STEM images of Co-Bi₃O₄Br-1, **e, f** STEM image and EDS mapping images of Co, Bi, O, and Br

to be approximately 0.91% and 0.36% at 380 and 400 nm, respectively. To determine the stability, the XRD, XPS valence-band spectra and TEM are employed for the used Co-Bi₃O₄Br-1 samples (Supplementary Fig. 10). No obvious variations of the crystal structure, electronic structure and morphology can be observed after the photoreaction, suggesting the favorable photostability.

Insight of the increased photocatalytic activity. To elucidate the origin of the increased photocatalytic activity, three elementary processes in photocatalytic CO₂ reduction namely light absorption, charge separation, and interfacial CO₂ catalysis are taken into consideration²⁴. After the incorporation of single-atom Co, the absorption in the visible light area can be improved due to the formed dopant energy levels of Co in the bandgap of Bi₃O₄Br (Supplementary Fig. 11a). The electrons in the valence band (VB) can be excited to the newly formed localized state of high-spin Co²⁺ (3d⁷). Moreover, the fully occupied electrons in t₂ levels of Co²⁺ can be easily excited to the unoccupied e levels

(d-d internal transitions), also contribute to the improved light absorption²⁵. The increased density of states of Co-Bi₃O₄Br in the bandgap through density functional theory (DFT) calculation further confirm the easily transition of photogenerated electrons to the new energy levels (Supplementary Fig. 11c, d). The corresponding bandgap energy of Bi₃O₄Br and Co-Bi₃O₄Br-1 are calculated to be 2.29 and 2.21 eV, respectively (Supplementary Fig. 11b). The detailed energy-level positions of VB edges determined from XPS VB spectra are both 1.06 eV (Supplementary Fig. 11e). Thus, the conduction band (CB) potentials of Bi₃O₄Br and Co-Bi₃O₄Br-1 are determined to be -1.23 and -1.15 eV, respectively, satisfying the thermodynamic requirements for CO₂ reduction to yield CO (Supplementary Fig. 11f).

To study the dynamic behaviors of photogenerated charge carriers in the prepared samples, ultrafast transient absorption (TA) spectra is employed. The biexponential fitting results are $\tau_1 = 12$ ps and $\tau_2 = 400$ ps for Bi₃O₄Br, while $\tau_1 = 11$ ps and $\tau_2 = 1$ ns for Co-Bi₃O₄Br-1 (Fig. 3c). Interestingly, the isolated

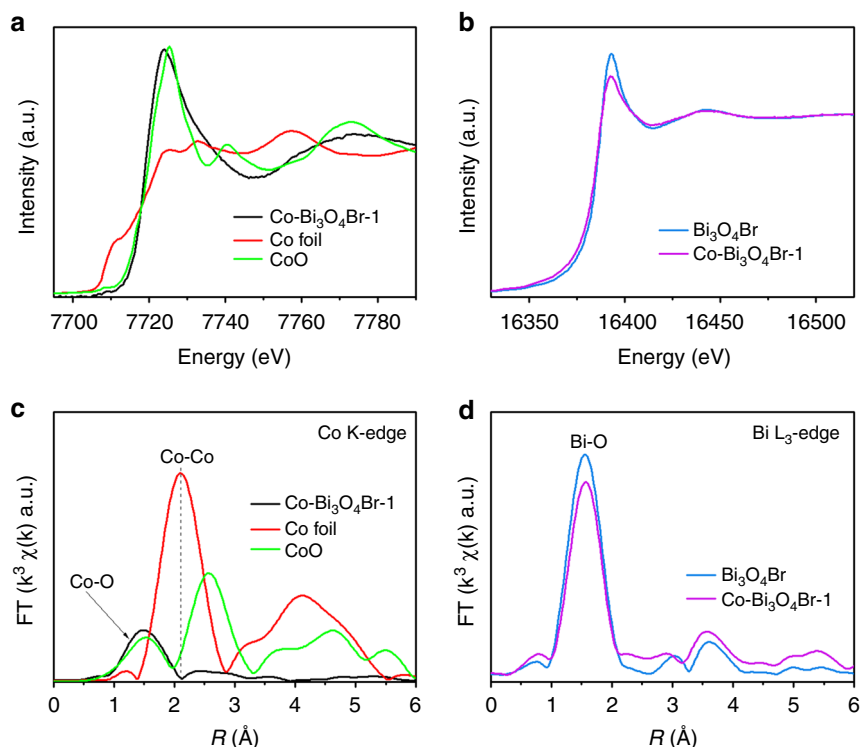


Fig. 2 Synchrotron radiation XAFS measurements. **a** Co K-edge XANES spectra, **b** Bi L₃-edge XANES spectra, EXAFS spectra of **c** Co K-edge and **d** Bi L₃-edge

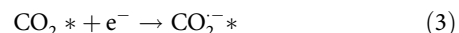
single-atom Co nearly not alter τ_1 , but endows a ~ 2.5 -fold increase for τ_2 . The τ_1 corresponded to electrons capture from CB into trap states within the bandgap, while the much slower decay component τ_2 represents the recombination between the trapped electrons and the VB holes¹⁶. The engineered isolated single-atom Co can supply trap states to capture more photogenerated electrons, while the more long-lived, trapped electrons afford more opportunities for CO₂ photoreduction. Moreover, time-resolved fluorescence emission decay spectra and surface photovoltage (SPV) spectroscopy are employed for further exploration (Supplementary Fig. 12a, b). The average fluorescence lifetime and SPV intensity of Co-Bi₃O₄Br-1 are much higher than that of Bi₃O₄Br atomic layers, respectively, further suggesting the increased charge separation efficiency in Co-Bi₃O₄Br. The isolated single-atom Co can work as charge separation center to trap the photogenerated electrons^{26,27}, and thus increase the carrier utilization efficiency toward redox reactions, also certified by the transient photocurrent responses and electrochemical impedance spectroscopy (Supplementary Fig. 12c, d).

To dive deep into the interfacial catalysis of CO₂ to yield CO, CO₂ surface adsorption, activation, and CO desorption processes are explored. Firstly, the CO₂ adsorption is generally considered as a prerequisite for CO₂ photoreduction reaction. The isolated single-atom Co²⁺ by replacing Bi³⁺ enables the Co-Bi₃O₄Br atomic layers to be more negatively charged, which may in favor of CO₂ adsorption on the surfaces¹⁶. It can be testified by the increased CO₂ adsorption capacity of Co-Bi₃O₄Br-1 relative to Bi₃O₄Br, as illustrated in Fig. 3d. Contact-angle measurement demonstrates that hydrophilicity may be not the crucial factor to affect CO₂ photoreduction reaction (Supplementary Fig. 13). Subsequently, the in situ Fourier transform infrared spectroscopy (FTIR) measurements are carried out to acquire in-depth understanding on the reaction intermediates (Fig. 3e). The peaks at 1256, 1337, and 1508 cm⁻¹ can be assigned to CO₂⁻, symmetric

O-C-O stretches of b-CO₃²⁻ and m-CO₃²⁻ groups, respectively^{28,29}. Notably the gradually increased peak at 1567 cm⁻¹ is ascribed to COOH* intermediate, a type of critical intermediate during the formation of CO₂ to CO^{6,29}. The band at ~ 1600 cm⁻¹ in the dark 30 min line is ascribed to the asymmetric O-C-O stretch of b-CO₃²⁻ groups. With the prolonged light irradiation time, this band is obscured by the significantly increased COOH* band. Lastly, the CO desorption is also considered as an important factor to decide the entirely photocatalysis efficiency. As shown from CO temperature-programmed desorption (TPD), the Co-Bi₃O₄Br-1 exhibits lower onset desorption temperature and higher overall amount of detected CO, revealing the formed CO* molecules can liberate from the Co-Bi₃O₄Br-1 surface much easier (Fig. 3f)²⁸. In addition, compared to the Bi₃O₄Br, a new lower-temperature desorption peak around 518 °C can be observed, implying the incorporated Co single atoms may favor the CO desorption, and this result is also certified by the calculated desorption free energy of CO (Fig. 4b).

Discussion

According to the analysis, the possible CO₂ reduction mechanism can be summarized as follows (Fig. 4a, Supplementary Fig. 14):



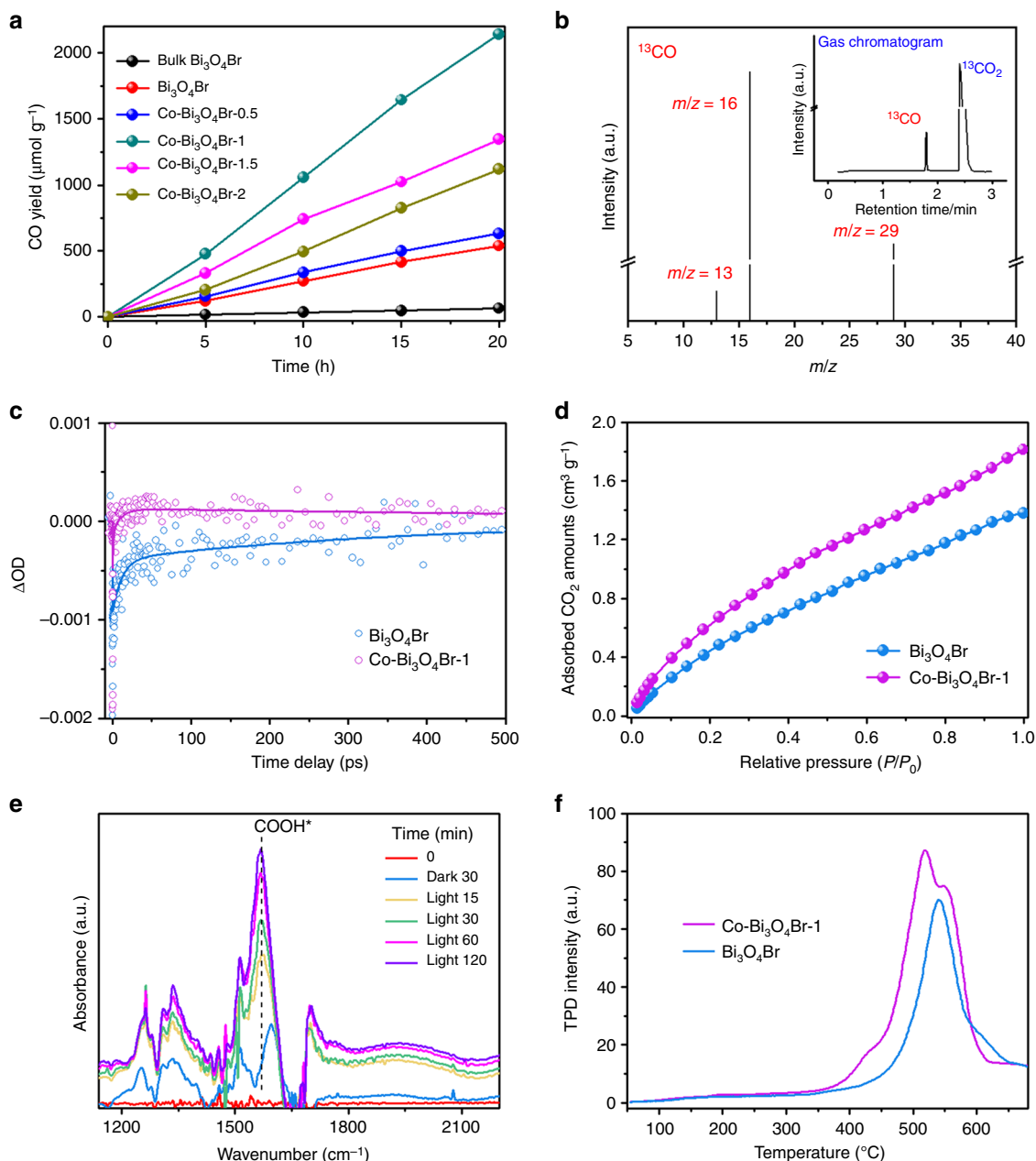


Fig. 3 Evaluation of CO₂ photoreduction performance and mechanism insight. **a** Photoreduction of CO₂ into CO over Bi₃O₄Br and Co-Bi₃O₄Br materials, **b** mass spectra of ¹³CO ($m/z = 29$) produced over Co-Bi₃O₄Br-1 in photoreduction of ¹³CO₂, **c** ultrafast TA spectra of Bi₃O₄Br and Co-Bi₃O₄Br, **d** CO₂ adsorption isotherms of Bi₃O₄Br and Co-Bi₃O₄Br-1, **e** in situ FTIR spectra for the CO₂ reduction process on the Co-Bi₃O₄Br-1, **f** CO TPD spectra of Bi₃O₄Br and Co-Bi₃O₄Br-1

where “*” on behalf of the adsorption state at the materials surface.

The CO₂ molecules are adsorbed on the surface of catalysts and the H₂O molecules are dissociated into hydroxyl and hydrogen ions. The CO₂* will be preferential combine with electron and hydrogen ion to form a carboxyl radical and then disintegrated into the adsorbed CO*³⁰. Eventually, the adsorbed CO* will desorb from the catalyst surface to form gaseous CO.

To explore the reactivity nature and CO₂ catalytic reduction cycle, DFT calculations are carried out (Fig. 4). Both the formation of COOH* and desorption of CO* for the Bi₃O₄Br are highly endergonic processes. The formation of adsorbed intermediate COOH* is found as the potential limiting step (Fig. 4b). However, the incorporated Co in Bi₃O₄Br can lower the CO₂

activation energy barrier through stabilizing the COOH* intermediates and tuning the rate-limiting step to be CO* desorption.

In conclusion, isolated single-atom Co are incorporated into the Bi₃O₄Br atomic layers to generate photocatalysts with superior activity for CO₂ reduction. Benefiting from the cooperation of ultrathin configuration and isolated single-atom Co, the Co-Bi₃O₄Br exhibits excellent photocatalytic activity toward CO₂ reduction to high selective yield CO, with a high formation rate of 107.1 μmol g⁻¹ h⁻¹, roughly 4 and 32 times higher than that of Bi₃O₄Br atomic layer and bulk Bi₃O₄Br, respectively. The Co single atoms in the Bi₃O₄Br benefit the charge transition, charge-carrier separation kinetics, CO₂ adsorption and activation. It can lower the CO₂ activation energy barrier through stabilizing the COOH* intermediates and tunes the rate-limiting step from

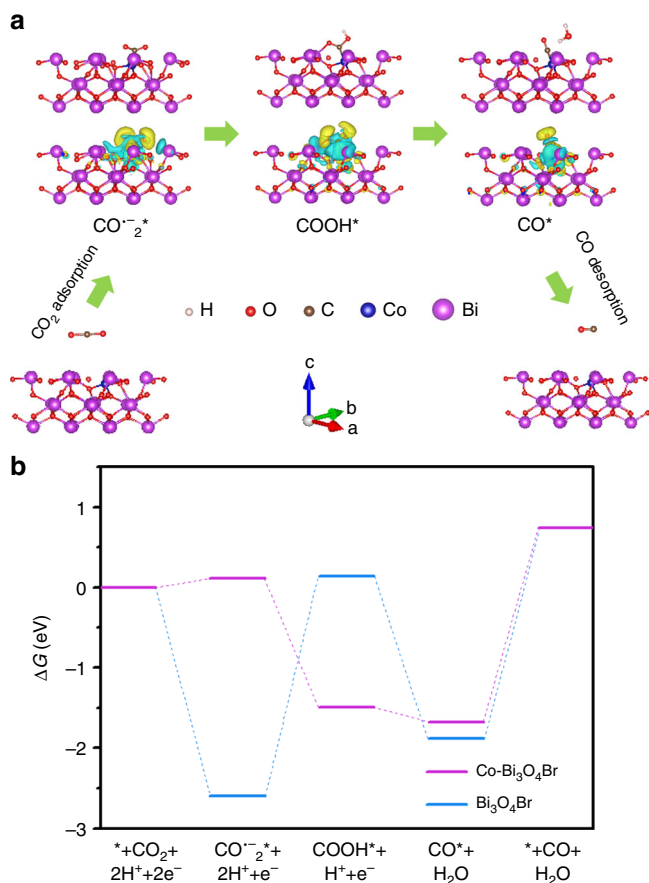


Fig. 4 Theoretical study. **a** Schematic representation of CO_2 photoreduction mechanism on the $\text{Co-Bi}_3\text{O}_4\text{Br}$, **b** free energy diagrams of CO_2 photoreduction to CO for the $\text{Bi}_3\text{O}_4\text{Br}$ and $\text{Co-Bi}_3\text{O}_4\text{Br}$

the formation of adsorbed intermediate COOH^* to CO^* desorption. Our findings shed light on the rational design of metal single atom incorporated atomic layer photocatalysts for robust solar-driven CO_2 conversion performances.

Methods

Synthesis of $\text{Co-Bi}_3\text{O}_4\text{Br}$ atomic layer. Totally, 0.5 mmol of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, 0.0054 g cobalt(II) acetate tetrahydrate and 0.2 g polyvinyl pyrrolidone (PVP, K30) were dispersed into 15 mL mannitol solution (0.1 mol/L) to achieve solution A. Totally, 0.5 mmol NaBr dissolved into 3 mL mannitol solution (0.1 mol/L) to obtain solution B. Subsequently, solution B was added into solution A under stirring. After 30 min stirring, NaOH solution (2 M) was employed to tune the pH value to 11.5. Then suspension was sealed in a 25 mL teflon-lined stainless-steel autoclave and heated in oven at 160°C for 24 h. After cooled down, the product was gathered, washed with deionized water and ethanol for several times, and dried. The calculated Co content relative to $\text{Bi}_3\text{O}_4\text{Br}$ is 1 wt%, and the sample is named as $\text{Co-Bi}_3\text{O}_4\text{Br-1}$. Adjusting the Co content to 0, 0.5, 1.5 and 2 wt% to prepare pure $\text{Bi}_3\text{O}_4\text{Br}$, $\text{Co-Bi}_3\text{O}_4\text{Br-0.5}$, $\text{Co-Bi}_3\text{O}_4\text{Br-1.5}$, and $\text{Co-Bi}_3\text{O}_4\text{Br-2}$ samples.

Synthesis of bulk $\text{Bi}_3\text{O}_4\text{Br}$. A total of 2 mmol Bi_2O_3 and 2 mmol BiOBr was sufficient mixed within 20 mL ethanol and stirred for 30 min. After drying, the powder was treated in muffle at 650°C for 10 h with the ramping rate of 5°C min^{-1} to achieve the product.

Characterizations. The powder X-ray diffraction (XRD) were recorded on a Shimadzu XRD-6000 X-ray diffractometer with monochromatized $\text{Cu K}\alpha$ radiation ($\lambda = 0.15418 \text{ nm}$). The XPS spectra were collected by an ESCALab MKII X-ray photoelectron spectrometer and all binding energies were calibrated by using the contaminant carbon ($\text{C}1s = 284.6 \text{ eV}$) as a reference. TEM images were collected on JEOL JEM-2100F. Aberration-corrected HAADF-STEM images were collected on a Nion Ultra STEM100 (USA) operated at 100 keV in Oak Ridge National

Laboratory. Co K-edge and Bi L_3 -edge X-ray absorption fine structure measurements were performed at the beamline 14W1 in Shanghai Synchrotron Radiation Facility, China. UV-vis diffuse reflection spectra of the $\text{Bi}_3\text{O}_4\text{Br}$ and $\text{Co-Bi}_3\text{O}_4\text{Br}$ samples were recorded on a UV-2450 UV-vis spectrophotometer (Shimadzu, Japan). The photoluminescence (PL) spectra were conducted using a Varian Cary Eclipse spectrometer (USA). CO_2 adsorption measurements were carried out through TriStar II 3flex gas adsorption analyzer (Micromeritics Instrument Corporation, USA). In situ FTIR were acquired using a Bruker vertex70. All electrochemical tests were performed on a CHI 660B electrochemical system (Chenhua Instruments) in conventional three-electrode cell with Pt as the counter electrode, and Ag/AgCl/sat. KCl electrode as the reference electrode. The ultrafast TA spectra were collected by using a femtosecond laser amplifier system (Spitfire Ace, Spectra Physics), which generates laser pulses with 800 nm central wavelength and $\sim 35 \text{ fs}$ pulse duration. The output beam was split into two beams. One was used to generate 400 nm pump light, and the other beam was focused into a sapphire plate, generating a broadband white light continuum probe beam. Both beams were focused onto the sample. After frequency resolved by a spectrograph, the excitation-induced transmission change for the probe light was collected by a home-built 46-channel synchronous digital lock-in amplifier. The isotope-labeled experiment was conducted using $^{13}\text{CO}_2$ instead of $^{12}\text{CO}_2$, and the products were analyzed through gas chromatography-mass spectrometry (7890A and 5975C, Agilent). CO TPD measurements were carried out on quantachrome autosorb-iQ-C chemisorption analyzer with a thermal conductivity detector.

Calculation details. The first-principles simulations are conducted using the Vienna ab initio simulation package, the projector augmented wave potentials are used as pseudopotentials to describe the interactions between valence electrons and ions. The Perdew-Burke-Ernzerhof functional of generalized gradient approximation is used to describe the exchange-correlation of valence electrons. The lattice parameters of bulk $\text{Bi}_3\text{O}_4\text{Br}$ is calculated first with the plane wave cutoff energy set as 500 eV and the k-point mesh set as $6 \times 6 \times 2$. The convergence criteria are 10^{-6} eV in electric relaxation energy and 10^{-4} eV in ionic relaxation energy. The optimized lattice parameter for bulk $\text{Bi}_3\text{O}_4\text{Br}$ was $5.78 \text{ \AA} \times 5.80 \text{ \AA} \times 19.03 \text{ \AA}$. To calculate the $\text{Bi}_3\text{O}_4\text{Br}$ layer slab, a $2 \times 2 \times 1$ supercell is created and a 20 Å vacuum layer is added on top of the supercell to avoid inter-layer interactions. Thus, the lattice parameter of the layer slab model is $11.56 \text{ \AA} \times 11.60 \text{ \AA} \times 39.03 \text{ \AA}$, with the plane wave cutoff energy set as 500 eV and the k-point mesh set as $3 \times 3 \times 1$. For the case of cobalt substitution and CO_2 molecule adsorption, all the parameters are remained same as that of $\text{Bi}_3\text{O}_4\text{Br}$ layer slab, except that the convergence criteria for ionic relaxation is changed to 0.02 eV/Å instead.

Photocatalytic CO_2 reduction. The CO_2 photoreduction performance evaluation of the $\text{Co-Bi}_3\text{O}_4\text{Br}$ samples was carried out in a 500 mL Labsolar-6A closed gas system (Perfectlight, China). Totally, 30 mg samples was added into 50 mL water and well dispersed. The system was vacuum-treated and then pumped into high-purity CO_2 with pressure of 0.08 MPa. Experiments were performed at 5°C with a circulating water system to prevent thermal catalytic effects. The amount of CO and CH_4 generated was determined using a gas chromatograph (Cotrun GC2002, FID) with a methanizer. A 300 W Xe lamp (Microsolar300, PerfectLight) was employed to provide light source. The apparent quantum efficiency is calculated according to the equation: apparent quantum efficiency = $100\% \times (\text{number of generated CO} \times 2) / \text{number of incident photons}$.

Data availability

The authors declare that the data supporting the findings of this study are available within the article and the Supplementary Information files.

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Author contributions

J.D., J.X.X., and Z.L. conceived and designed the experiments. J.D. prepared and characterized the photocatalysts and performed the photocatalytic experiments. S.Z.Y. and C.Z. carried out STEM. C.C., W.H., and S.Z.L. provided theoretical calculation and discussion. L.S. and S.M.C. analyzed the EXAFS data. M.L.D. and R.L. carried out the isotope-labeled experiment. Z.C., H.L.C., and Y.X.W. carried out the TA spectra. J.X. and H.M.L. discussed the results and commented on the paper. J.D. wrote the paper, J.X.X. and Z.L. revised the paper.

Additional information

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