Supporting Information Single-Atom Fe Triggers Superb CO₂ Photoreduction on a Bismuth-Rich Catalyst

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Materials: Bi(NO₃)₃·5H₂O, Fe(NO₃)₃·9H₂O, KI, ethylene glycol and ethanol were purchased from Aladdin Chemical Co., Ltd., and all of the reagents used without any further purification.

Synthesis: The preparation process is as follows: 0.73 g Bi(NO₃)₃·5H₂O and 0.166 g KI was dissolved in 10 mL ethylene glycol and 30 mL ethanol, respectively. KI solution was added into the Bi(NO₃)₃·5H₂O solution with continuously magnetic-stirring and ultrasonic-dispersing for 0.5 h. Then 0, 7.5, 30, 60 and 90 mg Fe(NO₃)₃·9H₂O were added to the above mixed solution, respectively. The mixture was transferred into a 50 mL Teflonlined stainless autoclave to perform a hydrothermal process at 180 °C for16 h. After the autoclave cooled to room temperature, the resulting samples were collected by washing three times with water and ethanol, and finally drying at 80 °C. The obtained samples were labeled as Bi4O₅I₂, Bi4O₅I₂-Fe7.5, Bi4O₅I₂-Fe15, Bi4O₅I₂-Fe30, Bi4O₅I₂-Fe60 and Bi4O₅I₂-Fe90, respectively. The synthesis of Fe-doped Bi4O₅I₂ without Bi decorating is similar to that of Bi4O₅I₂-Fe30 by tuning the solvothermal temperature at 150 °C.

Characterization: The X-ray diffraction patterns (XRD) were performed on a Bruker D8 diractometer using Cu Ka radiation, and the scanning region was from 5° to 80° with the scan rate of 6 min⁻¹. The morphologies of the samples were obtained by QUANTA200 FEI Emission Scanning Electron Microscope (FESEM). The transmission electron microscopy (TEM) and high resolution TEM (HRTEM) images were observed by JEOLJEM-2100F (UHR). Aberration-corrected HAADF-STEM images were collected on a Titan Cubed Themis G201 operated at 300 keV. X-ray photoelectron spectroscopy (XPS) measurements were carried out by Thermo Scientific ESCALAB 250XI X ray Photoelectron Spectrometer (Al Ka, 150 W, C 1s 284.8 eV). UV-vis diuse reflectance spectroscopy (DRS) of samples was characterized by a UV-vis spectrometer (Perkin Elmer, Lambda 650 s, BaSO4 as a reference). Electron paramagnetic resonance (EPR) spectra were recorded at room temperature on a Bruker model ESR JES-FA200 spectrometer. Time-resolved PL spectra recorded by a FLS980 multifunction steady state and transient state fluorescence spectrometer (Edinburgh Instruments, room temperature). The surface photovoltage (SPV) spectra were obtained on a laboratory-built surface photovoltage spectrometer. A 500 W xenon lamp equipped with a monochromator was employed used as the light source. A phase-locked amplifier (SR830-DSP, SR830, Stanford research systems, Inc.) synchronized with a light chopper (SR540, Stanford research systems, Inc.) was utilized to amplify the photovoltage signal. The CO₂ adsorption was measured using Quantachrome Autosorb-IQ automated gas sorption systems at 77 K. The Fe content of the sample was determined by elemental analysis of apples by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) in colloidal dispersions. The work function measurement was performed on a SKP 5050 K kelvin probe measurement system. The X-ray absorption fine structure spectra (XAFS) were investigated in X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) regions for Fe LIII-edge. The EXAFS experiments were collected at BL14W beamline in Shanghai Synchrotron Radiation Facility

(SSRF). The storage rings of SSRF was operated at 3.5 GeV with a stable current of 200 mA. Using Si(111) double-crystal monochromator, the data collection were carried out in fluorescence mode using Lytle detector. All spectra were collected in ambient conditions. The Doppler velocity of the spectrometer was calibrated with respect to α -Fe foil. The ¹³CO₂ isotope was measured on the British Hiden automatic quantitative analysis online mass spectrometer (HPR-20 R&D).

Photocatalytic CO₂ reduction: The photocatalytic CO₂ reduction experiment was tested at room temperature. In a typical measurement, 0.05 g photocatalyst was evenly dispersed on a quartz glass dish with an area of 28.26 cm² in a 350 mL reactor, and 5 mL distilled water was added at the bottom. Before the irradiation, the reactor was sealed with Ar flowing and high-purity CO₂ (1 ml) was then injected into the reactor with a magnetic stirring to obtain a uniform CO₂ atmosphere. A 300 W xenon lamp (PLS-SXE300C, Beijing Perfect light Technology Co., Ltd., China) was used as light source. During irradiation, gas (1 mL) was extracted with a syringe every 30 min and measured with a gas chromatograph (GC 9790II, Zhejiang Fuli Analytical Instrument Co., Ltd. China) equipped with a flame ionization detector (FID) detector. The amounts of CO and CH₄ were qualitatively analyzed according to the standard curves. The apparent quantum efficiency (AQE) was detected under the same photocatalytic reaction condition and calculated to the equation below:

AQE= number of reacted electrons/number of incident photons×100%

= (number of CO molecules×2+number of CH₄ molecules×8)/number of incident photons×100%

Photoelectrochemical measurement: The electrochemical impedance spectra (EIS), transient photocurrent responses and Mott–Schottky plots of the samples were determined using a CHI660D electrochemical working station (CHI Instruments, Shanghai, China). FTO glass with coated the prepared samples, a platinum wire and Ag/AgCl electrode were used as the working electrodes, counter electrode and reference electrode, respectively. A 300 W Xe lamp was utilized as the light source and Na₂SO₄ (0.5 M) aqueous solution was used as the supporting electrolyte throughout the photocurrent measurements.

In-situ Fourier transform infrared spectrometer (FT-IR) analysis: In situ Fourier transform infrared spectroscopy (FT-IR) was conducted on a Nicolet IS-50 instrument. The sample was placed into an in-situ Harrick IR cell, and 1 atm CO₂ and H₂O vapors were introduced into the cell and fiber source (FX300, Beijing Perfect Light Technology Co., Ltd., Beijing, China) through the CaF₂ window of the cell. Before the measurement, the samples were degassed at 423 K for 4 h. The baseline was obtained before the sample reached CO₂ adsorption equilibrium within 1 h.

DFT theoretical calculations: The first principles calculations were performed based on the density functional theory (DFT) simulations with the Vienna ab initio simulation package (VASP). Perdew-Burke-Ernzerhof (PBE) exchangecorrelation functional within a generalized gradient approximation (GGA) and the projector augmented-wave (PAW) potential were employed.¹⁻³ Lattice parameters were fully relaxed. Geometry of crystal is fully optimized before the electron structure and total energy calculation. The free energy of the intermediates is calculated as: $G{=}E(intermediate^*){+}ZPE(intermediate^*){-}TS(intermediate^*).$



Figure S1. The XRD patterns of Bi4O5I2, Bi4O5I2-Fe15, Bi4O5I2-Fe30 and Bi4O5I2-Fe60.



Figure S2. The magnified XRD patterns of Bi₄O₅I₂, Bi₄O₅I₂-Fe15, Bi₄O₅I₂-Fe30 and Bi₄O₅I₂-Fe60.



Figure S3. SEM images of as-obtained samples. (a) Bi₄O₅I₂, (b) Bi₄O₅I₂-Fe7.5, (c) Bi₄O₅I₂-Fe15, (d) Bi₄O₅I₂-Fe30, (e) Bi₄O₅I₂-Fe60, (f) Bi₄O₅I₂-Fe90 and (g) the EDS spectrum image of Bi₄O₅I₂-Fe30 taken from the corresponding region in d.



Figure S4. TEM images of Bi₄O₅I₂ (a,b) and Bi₄O₅I₂-Fe30 (c,d).



Figure S5. HRTEM image (a) and the corresponding profile of the lattice distance of

(303) and (020) facet over Bi₄O₅I₂-Fe30 (b).



Figure S6. The HRTEM image of Bi₄O₅I₂-Fe30 nanosheet on side view.



Figure S7. The HRTEM image of Bi₄O₅I₂-Fe30 nanosheet.



Figure S8. XPS spectra of Bi₄O₅I₂ and Bi₄O₅I₂-Fe30. (a) The survey XPS spectrum, (b) Bi 4f, (c) O 1s, (d) I 3d.



Figure S9. Aberration-corrected HAADF-STEM images of Bi₄O₅I₂-Fe30.



Figure S10. The calculated formation energy of Fe incorporate with substituted and interval form.



Figure S11. Atomic structure Bi₄O₅I₂ without Fe atom incorporating.



Figure S12. The charge density difference of Bi₄O₅I₂ with Fe atom incorporating.



Figure S13. The DRS spectra of $Bi_4O_5I_2$ samples with different Fe atom content.



Figure S14. The plots of $(ahv)^{1/2}$ vs. photon energy.



Figure S15. The photographs of $Bi_4O_5I_2$ samples with different single Fe atom content.



Figure S16. The band structure of $Bi_4O_5I_2$ and Fe atom implanted in $Bi_4O_5I_2$.



Figure S17. XRD pattern of Bi₄O₅I₂-Fe30-150.



Figure S18. SEM images (a,b) and corresponding elemental mapping images of Bi, O,

I and Fe (c-g) of Bi₄O₅I₂-Fe30-150.



Figure S19. Mott-Schottky curve of Bi₄O₅I₂-Fe30-150.



Figure S20. Illustration of the charge transfer process.



Figure S21. Time-resolved fluorescence decay plots of Bi₄O₅I₂ and Bi₄O₅I₂-Fe30.



Figure S22. CO and CH₄ selectivity over Bi₄O₅I₂ with different Fe content.



Figure S23. The corresponding gas chromatograms under different conditions over Bi₄O₅I₂-Fe30 for 2 h.



Figure S24. AQE of Bi₄O₅I₂-Fe30 and Bi₄O₅I₂ under 365, 400, 420 and 500 nm monochromatic light.



Figure S25. The rate of CO and CH₄ generation over Bi₄O₅I₂-Fe30, Bi₄O₅I₂-Fe30-150 and Bi₄O₅I₂.



Figure S26. Four recycle experiments of Bi₄O₅I₂-Fe30 for CO and CH₄ generation.



Figure S27. In situ FT-IR spectra of Bi₄O₅I₂-Fe30 at different time in the region of

2000-2600 cm⁻¹.



Figure S28. In situ FT-IR spectra of $Bi_4O_5I_2$ -Fe30 at different time in the region of

3400-4000 cm⁻¹.



Figure S29. In situ FT-IR spectra of Bi₄O₅I₂ and Bi₄O₅I₂-Fe30 under illumination for 60 min in the region of 1380-1800 cm⁻¹.





Figure S30. The CO₂ adsorption on pure Bi₄O₅I₂.



Figure S31. The CO₂ adsorption on Bi₄O₅I₂ with introducing single atom Fe.



Figure S32. The structures of various CO2 reduction products on Bi4O5I2 and Bi4O5I2-Fe30 surface.

Sample	τ1 (ns)	τ2 (ns)	τ3 (ns)	A1 (%)	A2 (%)	A3 (%) av	lifetime (ns)
Bi4O5I2	4.02	0.29	77.52	13.87	58.96	27.17	0.27
Bi4O5I2-Fe30	4.39	84.27	0.25	12.88	33.86	53.26	0.34

Table S1. Time-resolved PL decay fit parameters of $Bi_4O_5I_2$ -Fe30 and $Bi_4O_5I_2$.

Table S2.	Comparison	n of TiO2, g	g-C3N4, C	dS and E	Bi-based	photocatal	ysts fo	r CO2
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Photocatalysts	Light source	CO (µmol g ⁻¹ h ⁻¹)	CH4 (µmol g ⁻¹ h ⁻¹)	Refs.
TiO ₂	300 W Xe lamp	no	1.35	4
g-C3N4	300 W Xe lamp	1.97	1.94	5
CdS	300 W Xe lamp λ>400 nm	0.2	0.038	6
Ultrathin Bi ₂ WO ₆	300 W Xe lamp	no	0.41	7
Reduced	15 W daylight			0
graphene oxide	bulb	no	0.258	8
BiOCl with oxygen vacancies	300 W Xe lamp	1.01	0.15	9
Ultrathin BiOBr	300 W Xe lamp λ>400 nm	1.68	0.16	10
Few-layed BiOI	300 W Xe lamp λ>420 nm	0.51	0.18	11
C-doped Bi24O31Cl10	300 W Xe lamp	2.54	no	12
Hollow Bi ₄ O ₅ Br ₂	300 W Xe lamp	3.16	0.5	13
CeO ₂ /g-C ₃ N ₄	300 W Xe lamp	11.8	13.88	14
NiO/g-C3N4	300 W Xe lamp	4.17	no	15
WO ₃ /CdS	300 W Xe lamp λ>420 nm	no	1.02	16
CuInS ₂ /TiO ₂	350 W Xe lamp	no	2.5	17
Atomically-thin Bi2MoO6	300 W Xe lamp	3.62	no	18
Defective BiOBr	500 W Xe lamp λ>400 nm	no	0.486	19
MXene/Bi ₂ WO ₆	300 W Xe lamp	no	1.78	20
Ultrathin Bi4O5Br2	300 W Xe lamp λ>400 nm	2.73	2.04	21
BON-Br	300 W Xe lamp	8.12	no	22
BiOIO3 nanoplates	300 W Xe lamp	5.42	no	23
CdS/BiVO ₄	300 W Xe lamp λ>400 nm	0.48	1.85	24
Bi4O5I2-Fe30	300 W Xe lamp	23.77	4.98	This work

conversion

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