Electronic Supporting Information for

Engineering fast Ti electron channels to single-atom Fe for enhanced CO₂ photoreduction

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Experimental Section

Synthesis of Ti₃AlC₂

Ti₃AlC₂ powders were prepared by mixing commercial Ti₂AlC powders (Kanthal, Sweden) with TiC in a 1:1 molar ratio (after adjusting for the ~10 wt% Ti₃AlC₂ already present in the commercial powder) followed by ball milling for 1 day. The mixture was placed in an alumina boat and heated at a rate of 5 °C/min under continuous Ar flow to 1450 °C and held at that temperature for 1 h. The resulting loosely sintered brick was ground with a TiN-coated milling bit and sieved through a 400 mesh sieve, producing a powder with a particle size less than 38 μ m.

Synthesis of Ti_{3-x}C₂T_y

0.9999 g of LiF (97%, Alfa Aesar), 1.0000 g of sieved Ti_3AlC_2 powders were added into 10 mL of concentrated HCl solution (12 M, Tianjin Fuyu Fine Chemical Co., Ltd). The mixture was stirred in a 35 °C oil bath for 24 hours. The solid product was washed several times with deionized water, and centrifuged at 3500 rpm for 3 min each time until the color of the supernatant was cyanblack. After centrifugation, the solid product was mixed with 30 mL of deionized water and sonicated with Ar gas bubbling under ice bath for 1 h. The resulting suspension was centrifuged at 4000 rpm for 50 minutes, and the supernatant was the suspension containing 2D $Ti_{3-x}C_2T_y$ flakes. The concentration of the resulting suspension can be determined by suction filtration. Typically, the concentration is about 15 mg mL⁻¹. Finally, the layered sheet $Ti_{3-x}C_2T_y$ was obtained by freezedrying for 48 h.

Synthesis of Fe₁/Ti_{3-x}C₂T_y

In a typical synthesis of $Fe_1/Ti_{3-x}C_2T_y$, the above Mxene suspension containing 140 mg $Ti_{3-x}C_2T_y$ was diluted into 30 mL dispersion in deionized water, and stirred into a homogeneous solution. Then, 4 mL of FeCl₃ (99%, Aladdin) solution (0.2 M) was slowly added dropwise to the just obtained $Ti_{3-x}C_2T_y$ solution with stirring. After 30 minutes of reaction, the mixture was centrifuged at 4000 rpm for 3 minutes. The resulting solid product was washed several times with deionized water until the supernatant was colorless, and finally freeze-dried for 48 h.

Characterization

XRD patterns were measured at room temperature on a Bruker D8 Advance Powder Diffractometer with Cu Ka radiation (scanning range 10-80°, scanning speed 5°/min, working voltage 40 kV). The scanning electron microscopy (SEM, Zeiss Supra55) operated at 10 kV was used to characterize the morphology and structure of all samples. TEM images of samples were obtained from a JEM 1200EX transmission electron microscope (JEOL, Japan) operated at 100 kV. The high-resolution TEM (HRTEM), high-angle annular dark-field scanning TEM (HAADF-STEM) and energy dispersive X-ray (EDX) mapping images were acquired with a JEM-2100F field emission electron microscope (JEOL, Japan) operating at an accelerating voltage of 200 kV. ICP-OES was determined by a Thermo Fisher IRIS Intrepid a system. X-ray photoelectron spectroscopy (XPS) was performed on a ULVAC PHI Quantera microscope, and the binding energies (BE) were calibrated by C 1s with BE of 284.8 eV. X-ray absorption spectroscopy (XAS) measurements were performed at the 1W1B station in Beijing Synchrotron radiation Facility (BSRF, China). The UV-Vis diffuse reflection spectra were recorded using a Double Beam UV-Visible Spectrophotometer (TU-1901, China). Electron paramagnetic resonance (EPR) tests were carried out on a Model A300-10/12 EPR spectrometer (Bruker, Germany). The signals of •OH and O₂⁻ were detected under a 300 W Xe lamp irradiation using 5,5-dimethyl-1-pyrroline N-oxide (DMPO) as the radical trapping agent. The photoluminescence (PL) spectra of the samples were analysed on an Edinburgh FLS1000 transient steady-state fluorescence spectrometer, where the excitation wavelength, slit width and other parameters were set identically. N₂ adsorption/desorption isotherm curves were collected at 77 K on a Quantachrome SI-MP Instrument. The Brunauer-Emmett-Teller (BET) surface area and pore size of the samples ware estimated based on the N₂ adsorption-desorption experiments. CO₂ temperature-programmed desorption (CO₂-TPD) curves were measured on a Micromeritics Autochem II 2920 instrument. The concentration of desorbed CO₂ was determined by a thermal conductivity cell detector over a temperature rise range of 50-600 °C.

Photocatalytic CO₂ reduction

The photocatalytic CO_2 reduction process was carried out by gas-solid phase catalysis in a closed cycle system equipped with vacuum tubes. After fully grinding and ultrasonic in a small amount of water, the mixture containing 10 mg photocatalyst sample and 2 mg $[Ru(bpy)_3]Cl_2 \cdot 6H_2O$ (as photosensitizer) were uniformly dispersed and fixed on the porous quartz

fiber membrane of the tripod and placed in the reaction cell. Then 3 mL DI water was added into the reaction cell. After vacuuming, 60 kpa CO_2 was introduced into the system, and the light source was 300 W Xe lamp. Samples were taken from the reaction cell every 30 minutes and the gas product composition was analyzed in a gas chromatograph (GC-7890B, Agilent, America) equipped with a flame ionization detector (FID) and a thermal conductivity detector (TCD). The FID channel mainly detects the signals of carbon products such as CH_4 and CO, and the TCD channel mainly detects the signals of H_2 , O_2 and N_2 .

In the stability test, after the end of one cycle, 2 mg of photosensitizer was added to the sample surface, and then 3 mL of pure water and sufficient CO_2 were re-injected to the reaction cell before the next cycle of irradiation reaction.

Photocatalytic H₂O₂ evolution

To facilitate the detection of H_2O_2 , the photocatalytic reaction was carried out in a Schlenk tube (10 mL). In the Schlenk tube, 5 mg of catalyst was dispersed in 3 mL of pure water, and the nozzle was sealed with a rubber plug. After vacuuming, a proper amount of CO_2 was introduced into the system. Then the Schlenk tube was fixed on the agitator, and the solution was stirred under light irradiation for 4 h. The light source was 300 W Xe lamp, and the reaction was performed at room temperature. The mixture after reaction was centrifuged, and the supernatant was titrated with Ce(SO₄)₂ to verify the existence of H_2O_2 .

Products calculation

The detected peak area was converted to the actual volume by the standard curve, and the production rate of the product (CO or CH₄) was calculated using the following equation:

$$Production \ rate_{(CO/CH_4)} = \frac{V_{(CO/CH_4)}}{22.4 \times M \times T}$$

Where V (mL) is the actual product volume converted by CO / CH_4 standard gas; M (g) is the mass of the catalyst; T (h) is the irradiation time.

The turnover number (TON) was calculated by^{1,2}

$$TON = \frac{number \ of \ reacted \ electrons}{Amount \ of \ catalyst} = \frac{2V_{co} + 8V_{CH_4}}{22.4 \times M \times T}$$

Photoelectrochemical measurements

Photoelectrochemical measurements were performed in a three-electrode cell connected to an electrochemical workstation (CHI760E) with a 300 W Xe lamp as the light source. The photocurrent response and EIS Nyquist plots of the as-prepared catalysts (with $[Ru(bpy)_3]Cl_2 \cdot 6H_2O$) were tested in 0.5 M Na₂SO₄ electrolyte solution. The sample-loaded fluoride doped tin oxide (FTO) conductive glass (2×1 cm²) was used as the working electrode, the platinum sheet electrode was used as the counter electrode, and the Ag/AgCl electrode was used as the reference electrode.

In-situ Fourier transform infrared (In-situ FTIR) spectroscopy

In-situ Fourier transform infrared (FTIR) measurements were conducted using the Thermo Scientifi Nicolet iS50 spectrometer equipped with an in-situ diffuse reflectance cell (Harrick) to identify and analyze the intermediates involved in the reaction. The sample was initially affixed to a scaffold within the reaction cell, followed by continuous purging of the catalyst surface in an Ar atmosphere for approximately 30 minutes. The baseline FTIR sampling was recorded to confirm the effective elimination of surface adsorbed impurities. The system was subsequently infused with moist CO_2 in the absence of light through a U-shaped tube containing deionized water. After reaching adsorption equilibrium on the catalyst surface (approximately 30 minutes), the pre-reaction FTIR data were collected as a reference. Then the reactor was exposed to UV-vis light, while FTIR spectra were collected continuously during the flow of wet CO_2 .

Computational details

A series of density functional theory (DFT) calculations were all done with the Vienna Ab initio Simulation Package (VASP).^{3,4} The electron-ion interaction was described using the projector augmented wave (PAW),⁵ and the kinetic energy cutoff for plane wave expansions was set to 450 eV. The electron exchange and correlation energies were treated within a generalized gradient approximation (GGA) in the Perdew-Burke-Ernzerhof (PBE) exchange-correlation.⁶ A DFT-D3 scheme of dispersion correction was used to describe the van der Waals (vdW)

interactions in molecule adsorption.⁷ The Brillouin zone was sampled using the Monkhorst-Pack $2\times2\times1$ sampling and the convergence criteria were 1×10^{-6} eV in structure optimization,⁸ and force convergence criterion of -0.02 eV/Å. The electron smearing width of $\sigma = 0.05$ eV was employed according to the Methfessel-Paxton technique. To avoid the interactions between two adjacent periodic images, the vacuum thickness was set to be 20 Å, and to simulate the effect of inside a solid, we fixed two-layer atoms at bottom.

The adsorption energy (E_{ad}) was calculated by subtracting the energies of the isolated adsorbate and the catalyst from the total energy of the adsorbed system:

 $E_{ad} = E_{slab + adsorbate} - E_{slab} - E_{adsorbate}$

Where $E_{slab+adsorbate}$ is the total energy of adsorbate as adsorbed steadily at the active site. E_{slab} and $E_{adsorbate}$ is the total energy of adsorbed surface and isolated adsorbate, respectively.

The charge density difference was evaluated using the formula $\Delta \rho = \rho$ (substrate + adsorbate) - ρ (adsorbate) - ρ (substrate), then analyzed by using the VESTA code.⁹



Supporting Figures and Tables

Fig. S1 XRD pattern of $Fe_1/Ti_{3-x}C_2T_y$.



Fig. S2 SEM images of (a) $Ti_{3-x}C_2T_y$ and (b) $Fe_1/Ti_{3-x}C_2T_y$.



Fig. S3 TEM images of (a) $Ti_{3-x}C_2T_y$ and (b) $Fe_1/Ti_{3-x}C_2T_y$.



Fig. S4 High-resolution Ti 2p XPS spectra of $Fe_1/Ti_{3-x}C_2T_y$ and $Ti_{3-x}C_2T_y$.



Fig. S5 High resolution XPS spectra of (a) C 1s and (b) O 1s in $Fe_1/Ti_{3-x}C_2T_y$ and pure $Ti_{3-x}C_2T_y$.



Fig. S6 k space EXAFS fitting curves of $Fe_1/Ti_{3-x}C_2T_y$.



Fig. S7 Time course of CH_4 evolution over $Fe_1/Ti_{3-x}C_2T_y$ and $Ti_{3-x}C_2T_y$.



Fig. S8 Time course of photoreduction-products evolution over pure [Ru(bpy)₃]Cl₂.



Fig. S9 (a-b) Time course of photoreduction-products evolution and (c) gas evolution rates over $Ti_{3-x}C_2T_y$ and $Fe_1/Ti_{3-x}C_2T_y$ without Ru.



Fig. S10 Calculated TONs over $Ti_{3-x}C_2T_y$, $Fe_1/Ti_{3-x}C_2T_y$ and pure $[Ru(bpy)_3]Cl_2$.



Fig. S11 Cyclic stability tests of CO_2 photoreduction over $Fe_1/Ti_{3-x}C_2T_y$ with irradiation for 4 h each cycle.



Fig. S12 Time course of (a) CO and (b) CH_4 evolution over $Fe_1/Ti_{3-x}C_2T_y$ under different reaction conditions before and after the UV-visible light irradiation.



Fig. S13 UV-vis spectrum of the reaction solution (RS) with addition of $Ce(SO_4)_2$ (red line). Pure $Ce(SO_4)_2$ solution (green line), pure $[Ru(bpy)_3]Cl_2$ solution (purple line) and their mixed solution (blue line) were used as control. Among them, the concentration of Ce^{4+} introduced was consistent (0.5 mM).



Fig. S14 EPR spectra of radical adducts trapped by DMPO in $Fe_1/Ti_{3-x}C_2T_y$ and $Ti_{3-x}C_2T_y$ dispersions before and after UV-visible light irradiation: (a) DMPO-O₂^{•-} formed in irradiated aqueous dispersions; (b) DMPO-•OH formed in irradiated methanol dispersions.



Fig. S15 UV-Vis spectra of the pure Ru and $Ti_{3-x}C_2T_y$ or $Fe_1/Ti_{3-x}C_2T_y$ with $[Ru(bpy)_3]Cl_2$. The absorbance has been normalized.



Fig. S16 N_2 adsorption/desorption isotherm curves of $Ti_{3-x}C_2T_y$ and $Fe_1/Ti_{3-x}C_2T_y$.



Fig. S17 DFT pore size distribution plots of (a) $Fe_1/Ti_{3-x}C_2T_y$ and (b) $Ti_{3-x}C_2T_y$.



Fig. S18 The increasing relation of FTIR signals of main adsorbed intermediates over $Fe_1/Ti_{3-x}C_2T_y$ surface with time during irradiation.



Fig. S19 The plots of different views for optimal structures of (a) $Ti_{3-x}C_2T_y$ and (b) $Ti_{3-x}C_2T_y *CO_2$, respectively.



Fig. S20 The plots of different views for optimal structures of (a) $Fe_1/Ti_{3-x}C_2T_y$ and (b) $Fe_1/Ti_{3-x}C_2T_y$ *CO₂, respectively.



Fig. S21 The plots of different views for optimal structures of (a) $Fe_1/Ti_{3-x}C_2T_y*CO_2-OH_{near}-1$, (b) $Fe_1/Ti_{3-x}C_2T_y*CO_2-OH_{near}-2$ and (c) $Fe_1/Ti_{3-x}C_2T_y*CO_2-OH_{far}$, respectively. Among them, $Fe_1/Ti_{3-x}C_2T_y*CO_2-OH_{near}-1$ and $Fe_1/Ti_{3-x}C_2T_y*CO_2-OH_{near}-2$ represent CO₂ adsorption at different -OH positions near Fe atoms, while $Fe_1/Ti_{3-x}C_2T_y*CO_2-OH_{far}$ represents CO₂ adsorption at -OH site far from Fe atoms.



Fig. S22 Charge density differences with (a) $Fe_1/Ti_{3-x}C_2T_y^*CO_2$ and (b) $Ti_{3-x}C_2T_y^*CO_2$, from up to down: top view and side view of 3D plot. The isosurface level set to 0.001 eÅ⁻³, where charge depletion and accumulation were depicted by cyan and yellow, respectively.

Table S1 Structural parameters of $Fe_1/Ti_{3-x}C_2T_y$ extracted from the EXAFS fitting. ($S_0^2=0.80$)

Sample	Scattering pair	CN	R(Å)	σ ² (10 ⁻³ Å ²)	$\Delta E_0(eV)$
Fe ₁ /Ti _{3-x} C ₂ T _y	Fe-C	4.0±0.2	2.11±0.02	5.7±0.8	2.9±0.7
	Fe-Ti	5.8±0.6	3.02±0.02	6.2±0.6	4.6±0.8

 S_0^2 is the amplitude reduction factor $S_0^2=0.8$; CN is the coordination number; R is interatomic distance (the bond length between central atoms and surrounding coordination atoms); σ^2 is Debye-Waller factor (a measure of thermal and static disorder in absorber-scatterer distances); ΔE_0 is edge-energy shift (the difference between the zero kinetic energy value of the sample and that of the theoretical model). R factor is used to value the goodness of the fitting.

	Catalysts	Reaction condition	Light source	Production rate	References
Gas-solid phase CO ₂ photoreduction	Fe ₁ /Ti _{3-x} C ₂ T _y + [Ru(bpy) ₃]Cl ₂	CO ₂ (g) and H ₂ O vapour	300 W Xe lamp	259.0 μmol g ⁻¹ h ⁻¹ for CO and 38.8 μmol g ⁻¹ h ⁻¹ for CH ₄	This work
	Cu ₁ N ₃ @PCN	CO ₂ (g) and H ₂ O vapour	300 W Xe lamp (λ≥420 nm)	~49.8 µmol g ⁻¹ h ⁻¹ for CO	Angew. Chem. Int. Ed. 2022, 61, e202207677
	Mn ₁ Co ₁ /CN	CO ₂ (g) and H ₂ O vapour	300 W Xe lamp (cut off infrared light)	47 μmol g ⁻¹ h ⁻¹ for CO	Angew. Chem. Int. Ed. 2022, 134, e202206579
	1Cu-mTiO ₂	CO ₂ (g) and H ₂ O vapour	300 W Xe arc lamp	~4.5 μmol g ⁻¹ h ⁻¹ for CH ₄ , ~0.9 μmol g ⁻¹ h ⁻¹ for CO and ~0.8 μmol g ⁻¹ h ⁻¹ for H ₂	ACS Catal. 2019, 9, 4824-4833
	Cu-CCN	CO ₂ (g) and H ₂ O vapour	Xe lamp	3.086 μmol g ⁻ ¹ h ⁻¹ for CO	ACS Nano 2020, 14, 10552-10561
	Ni ₅ -CN	CO ₂ (g) and H ₂ O vapour	Xe lamp (visible- light)		Small 2020, 16, 2002411
	K-CN	CO ₂ (g) and H ₂ O vapour	simulate visible-light	8.7 μmol g ⁻¹ h ⁻¹ for CO	ACS Sustainable Chem. Eng. 2020, 8, 8214-8222

Table S2 Summary of single-atom catalysts for CO2 photoreduction.

	IL/Co-bCN	CO ₂ (g) and H ₂ O vapour	300 W Xe lamp	$\begin{array}{c} 40.5 \ \mu mol \ g^{-1} \\ h^{-1} \ for \ CO \\ and \ 6.3 \ \mu mol \\ g^{-1} \ h^{-1} \ for \\ CH_4 \end{array}$	Nat. Commun. 2023,14, 1457
	Cu ₁ /TiO ₂	CO ₂ (g) and H ₂ O vapour	100 W Xe lamp with a 1.5 AM filter	$\begin{array}{c} 1416.9 \text{ ppm} \\ g^{-1} h^{-1} \text{ for} \\ \text{CH}_4 \text{ and } 64.2 \\ \text{ppm } g^{-1} h^{-1} \\ \text{ for } \text{C}_2\text{H}_6 \end{array}$	Energy Environ. Sci. 2022, 15, 601-609
	Zn SA-CoO NRs	CO ₂ (g) and H ₂ O vapour	300 W Xe lamp with a 1.5 AM filter	86.7 μmol g ⁻¹ h ⁻¹ for CO and 31.4 μmol g ⁻¹ h ⁻¹ for CH ₄	Adv. Funct. Mater. 2022, 32, 2109693
	Cu-SAs/TiO ₂	$\begin{array}{c} \text{CO}_2 \text{ (g),} \\ \text{H}_2\text{O} \\ \text{vapour and} \\ \text{O}_2(117.6 \\ \text{ppm}) \end{array}$	Xe lamp (320~850 nm)	23.11 μmol g ⁻ ¹ h ⁻¹ for CH ₄ and 13.71 μmol g ⁻¹ h ⁻¹ for CO	Appl. Catal. B 2023, 325, 122339
	Au/Co DSA- loaded CdS NPs (CAC2)	CO ₂ (g)	300 W Xe lamp (λ≥400 nm)	9.2 μmol g ⁻¹ h ⁻¹ for CO and 1.1 μmol g ⁻¹ h ⁻¹ for CH ₄	Adv. Mater. 2023, 35, 2306923
	Cu-SAEB	CO ₂ (g) and H ₂ O vapour	300 W Xe lamp	236.0 μmol g ⁻ ¹ h ⁻¹ for CO	Angew. Chem. 2023, 62, e202218460
	Ag/TiO ₂	CO ₂ (g) and H ₂ O vapour	300 W Xe lamp with a 1.5 AM filter	46.0 μmol g ⁻¹ h ⁻¹ for CH ₄	Energy Environ. Sci., 2024, 17, 518-530
Gas-liquid phase CO ₂ photoreduction	Co-Ti ₃ C ₂ T _x + [Ru(bpy) ₃]Cl ₂	$\begin{array}{c} 3 \text{ mL} \\ \text{CH}_3\text{CN}, 2 \\ \text{mL} \text{ H}_2\text{O}, 1 \\ \text{mL} \text{ TEOA} \\ \text{and} \text{ CO}_2 \\ \text{(g)} \end{array}$	300 W Xe lamp (λ≥420 nm)	$\begin{array}{c} 6061 \ \mu mol \ g^{-1} \\ {}^{1} \ h^{-1} \ for \ CO \\ and \ 2251 \\ \mu mol \ g^{-1} \ h^{-1} \\ for \ H_{2} \end{array}$	Cell Rep. Phys. Sci. 2021, 2, 100371

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	Ni-TpBpy + [Ru(bpy) ₃]Cl ₂	3 mL $CH_3CN, 1$ $mL H_2O, 1$ mL TEOA and CO_2 (g)	300 W Xe lamp (λ≥420 nm)	811.4 μmol g ⁻ ¹ h ⁻¹ for CO and 34 μmol g ⁻¹ h ⁻¹ for H ₂	J. Am. Chem. Soc. 2019, 141, 7615- 7621
	Mn SA-N-C+ [Ru(bpy) ₃]Cl ₂	$\begin{array}{c} 8 \text{ mL} \\ \text{CH}_3\text{CN}, 2 \\ \text{mL} \text{ H}_2\text{O}, 2 \\ \text{mL} \text{ TEOA} \\ \text{and} \text{ CO}_2 \\ \text{(g)} \end{array}$	300 W Xe lamp (λ>420 nm)	1470 μmol g ⁻ ¹ h ⁻¹ for CO and 1310 μmol g ⁻¹ h ⁻¹ for H ₂	Nano Energy 2020, 76, 105059
	Co–Bi ₃ O ₄ Br	50 mL H ₂ O and CO ₂ (g)	300 W Xe lamp	$107.1 \ \mu mol \ g^{-1} h^{-1}$ for CO and trace CH ₄	Nat. Commun. 2019, 10, 2840
	Co ²⁺ @C ₃ N ₄	3.2 mL CH ₃ CN, 0.8 mL TEOA and CO ₂ (g)	Halogen lamp (λ>420 nm)	5 μmol g ⁻¹ h ⁻¹ for CO	J. Am. Chem. Soc. 2018, 140, 16042- 16047
	Er _l /CN-NT	4 mL H ₂ O and CO ₂ (g)	300 W Xe arc lamp (λ>420 nm)	$\begin{array}{c} 47.1 \ \mu mol \ g^{-1} \\ h^{-1} \ for \ CO \\ and \ 2.5 \ \mu mol \\ g^{-1} \ h^{-1} \ for \\ CH_4 \end{array}$	Angew. Chem. Int. Ed. 2020, 59, 10651-10657
	Ni-OB-CN	5 mL H ₂ O and CO ₂ (g)	300 W Xe lamp	$\begin{array}{c} 22.1 \ \mu mol \ g^{-1} \\ h^{-1} \ for \ CO \\ and \ 8.7 \ \mu mol \\ g^{-1} \ h^{-1} \ for \\ CH_4 \end{array}$	Adv. Mater. 2021, 33, 2105482
	Fe-g-C ₃ N ₄	$\begin{array}{c} 100 \text{ mL} \\ \text{H}_2\text{O} \text{ and} \\ \text{CO}_2 \left(g \right) \end{array}$	300 W Xe lamp	0.5 μmol g ⁻¹ h ⁻¹ for CO	Phys. Chem. Chem. Phys. 2021 , 23, 4690-4699
	UiO-66-NH ₂ -Zn SAs	5 mL H ₂ O and CO ₂ (g)	300 W Xe arc lamp	$\begin{array}{c} 40.2 \ \mu mol \ g^{-1} \\ h^{-1} \ for \ CO \\ and \ 5.0 \ \mu mol \\ g^{-1} \ h^{-1} \ for \\ CH_4 \end{array}$	J. Mater. Chem. A 2022, 10, 23666-23674

	Pt-SA/CTF-1	$\begin{array}{c} 10 \text{ mL} \\ \text{H}_2\text{O}, 2.075 \\ \text{mL TEA} \\ \text{and CO}_2 \\ \text{(g)} \end{array}$	300 W Xe lamp (λ≥420 nm)	~4.7 μ mol g ⁻¹ h ⁻¹ for CH ₄ and ~1.4 μ mol g ⁻¹ h ⁻¹ for CO	Chem. Eng. J. 2022, 427, 131018
	Cu-SA/CTF	$5 \text{ mL H}_2\text{O},$ 15 mmol TEA and CO ₂ (g)	300 W Xe lamp (λ≥420 nm)	32.56 μmol g ⁻¹ h ⁻¹ for CH ₄ and 2.24 μmol g ⁻¹ h ⁻¹ for CO	Nano Res. 2022, 15, 8001-8009
	Au ₁ /ZnIn ₂ S ₄ + [Ru(bpy) ₃]Cl ₂	3 mL CH ₃ CN, 1 mL H ₂ O, 1 mL TEOA and CO ₂ (g)	300 W Xe lamp (λ>420 nm)	275 μ mol g ⁻¹ h ⁻¹ for CH ₄ , ~80 μ mol g ⁻¹ h ⁻¹ for CO and ~250 μ mol g ⁻¹ h ⁻¹ for H ₂	Angew. Chem. Int. Ed. 2022, 61, e202209446
	Fe SAS/Tr- COF+ [Ru(bpy) ₃]Cl ₂	$\begin{array}{c} 3 \text{ mL} \\ \text{CH}_3\text{CN}, 1 \\ \text{mL} \text{ H}_2\text{O}, 1 \\ \text{mL} \text{ TEOA} \\ \text{and} \text{ CO}_2 \\ \text{(g)} \end{array}$	300 W Xe lamp (λ≥420 nm)	980.3 μmol g ⁻¹ h ⁻¹ for CO and 36.6 μmol g ⁻¹ h ⁻¹ for H ₂	J. Am. Chem. Soc. 2022, 144, 17097–17109
	Cu-Bpy-COF	10 mL DMF or H_2O , 1 mL TEA and CO_2 (g)	300 W Xe lamp (λ>420 nm)	70.0 μ mol g ⁻¹ h ⁻¹ for CH ₄ and 6.4 μ mol g ⁻¹ h ⁻¹ for CO in H ₂ O; 40.8 μ mol g ⁻¹ h ⁻¹ for CO and no CH ₄ in DMF	Small 2023, 19, 2300035
	Ni/SOM-ZIF-8+ [Ru(bpy) ₃]Cl ₂	$\begin{array}{c} 6 \text{ mL} \\ \text{CH}_3\text{CN}, 2 \\ \text{mL} \text{ H2O}, \\ 2 \text{ mL} \\ \text{TEOA and} \\ \text{CO}_2 \left(g \right) \end{array}$	300 W Xe lamp (λ≥400 nm)	4200 μmol g ⁻ ¹ h ⁻¹ for CO	ACS Catal. 2023, 13, 6630-6640

Species	$E_{slab+}^{CO_2}$ (eV)	E _{slab} (eV)	$\mathbf{E}^{CO_2}(\mathbf{eV})$	E _{ad} (eV)
Ti _{3-x} C ₂ T _y *CO ₂	-1815.22	-1791.57	-22.96	-0.69
$Fe_1/Ti_{3-x}C_2T_y^*CO_2$	-1740.03	-1714.81	-22.96	-2.26
$Fe_1/Ti_{3-x}C_2T_y*CO_2-OH_{near}-1$	-1737.42	-1714.81	-22.96	0.34
$Fe_1/Ti_{3-x}C_2T_y^*CO_2$ -OH _{near} -2	-1737.39	-1714.81	-22.96	0.37
$Fe_1/Ti_{3-x}C_2T_y^*CO_2$ -OH _{far}	-1738.39	-1714.81	-22.96	-0.62

Table S3 Total energy of CO₂ adsorption at different interfaces.

 E_{slab+} ^{CO₂} is the total energy of CO₂ as adsorbed steadily at the active site; Eslab and E^{CO₂} is the total energy of adsorbed surface and isolated CO₂, respectively; Ead is the adsorption energy of CO₂ on the surface. Fe₁/Ti_{3-x}C₂T_y*CO₂-OH_{near}-1 and Fe₁/Ti_{3-x}C₂T_y*CO₂-OH_{near}-2 represent the adsorption of CO₂ on different -OH sites near Fe atoms. Fe₁/Ti_{3-x}C₂T_y*CO₂ -OH_{far} represents the adsorption of CO₂ on -OH sites away from Fe atoms.

References

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