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Electronic Supporting Information (ESI)

Light intensity–directed selective CO₂ photoreduction using iron(0)–zirconium dioxide photocatalyst

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1. Introduction

First-row transition metals such as Ti, V, Cr, Mn, Fe, Co, and Ni present promising inexpensive alternatives as photocatalytic active

components for CO_2 reduction, potentially replacing currently preferred but expensive Cu, Ag, and Pt metals. $^{\rm S1,S2}$

Table S1 Reported photocatalysts that utilize Fe as active sites.

Entry	Photocatalyst	Reducing agent	Product	duct Formation rate		
а	Fe-MIL-100	TEOA	Formate	150 µmol h ⁻¹ g _{cat} ⁻¹	S3	
b	g-C₃N₄–Fe-MIL-88B		CO	13 μ mol h ⁻¹ g _{cat} ⁻¹	S4	
С	FeO _x –In ₂ O ₃		CO	4.8 mmol h ⁻¹ g _{cat} ⁻¹	S5	
d	Fe-TCPP–MOF		CO	10 mmol h ⁻¹ g _{cat} ⁻¹	S6	
е	Fe-N-MIL-101-rGO	H ₂ O			S7	
f	Fe–Ti-MXene	H ₂ O	CO	260 µmol h ⁻¹ g _{cat} ⁻¹	S8	
g	g-C₃N₄–Fe-PCN-222		CO		S9	
h	En TiO		CO,	21 µmol h ⁻¹ g _{cat} ⁻¹ ,	\$10	
n	Fe-TIO ₂		CH ₄	40 μ mol h ⁻¹ g _{cat} ⁻¹	510	
i	FeO _x –MOF		CO	170 µmol h ⁻¹ g _{cat} ⁻¹	S11	
j	Fe–COF	H ₂ O	CO	4.0 mmol h ⁻¹ g _{cat} ⁻¹	S12	
k		BIH	Formate,	4.1 mmol h ⁻¹ g _{cat} ⁻¹ ,	\$13	
ĸ	re-bpy-cor		CO	2.1 mmol h ⁻¹ g _{cat} ⁻¹	515	
I	Fe ₂ O ₃ –Ti MXene	H ₂ O	CO	240 µmol h ⁻¹ g _{cat} ⁻¹	S14	
m	Fe-N₃tpy	TEA	CO	6.2 mmol h ⁻¹ g _{cat} ⁻¹	S15	
n	$Fe_2O_3@In_2S_3$	H ₂ O	CO	43 µmol h⁻¹ g _{cat} ⁻¹	S16	
0	NH ₂ -MIL-101(Fe)@Ti ₃ C ₂		CO	56 µmol h⁻¹ g _{cat} ⁻¹	S17	
р	NH ₂ -MIL-101(Fe)@Bi ₂ MoO ₆	TEOA	CO	67 µmol h⁻¹ g _{cat} ⁻¹	S18	
q	Fe/Ti-BPDC MOF		HCO ₂ H	700 µmol g ⁻¹ h ⁻¹	S19	
r	Fe₃ oxide–MOF	IPA	CO	140 µmol h ⁻¹	S20	
S	Fe–Bi₅O ₇ I	H ₂ O	CO	12 µmol·g ^{−1} ·h ^{−1}	S21	
t	Fe-Bi ₂ O ₂ S		CH ₄	1.7 μmol g ⁻¹ h ⁻¹	S22	
u	Ferrocene–Ti cluster	TEOA	Formate	40 µmol g ⁻¹ h ⁻¹	S23	
v	Fe(BPAbipy)	BIH	СО	52 µmol h⁻¹	S24	

2. Experimental section

The Fe^0-photocatalyst was synthesized via the following procedure. ZrO_2 (0.50 g, specific surface area: 100.5 m² g⁻¹; Type JRC-ZRO-7,

Catalysis Society of Japan) was dispersed in deionized water (100 mL; conductivity <0.055 μ S cm⁻¹, model RFU424TA, Advantec, Japan) along with Fe(NO₃)₃·9H₂O (0.2935 g). The suspension was ultrasonicated for 20 min before the dropwise addition of NaBH₄ (0.3298 g) dissolved in deionized water (20 mL) over 5 min. Major impurity of the ZrO₂ sample was Hf: 0.55 wt% in sample based on our X-ray absorption spectroscopy study. The reaction mixture was

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COMMUNICATION

stirred at 900 rotations per minute (rpm) for 10 min, followed by filtration using a membrane filter (pore size = $0.1 \,\mu$ m; Omnipore Type JVWP04700, Merck–Millipore, Darmstadt, Germany) and washed five times with deionized water (50 mL). The resulting solid was initially dried at 373 K for 12 h, then further dried at 373 K for an additional 24 h. Finally, the sample was heated under H₂ (21.7 kPa) at 973 K for 1 h. The obtained photocatalyst is referred to as Fe⁰ (7.5 wt %)–ZrO₂-973R.

CO photoreduction tests at the gas/solid interface were performed using 20 mg of the photocatalyst. The reaction was conducted in the presence of 13 CO₂ (2.3 kPa, chemical purity >99.9%; 99.0% 13 C, 0.1% 17 O, 0.7% 18 O, Cambridge Isotope Laboratories, Inc., Tewksbury, MA, USA) and H₂ (2.3–21.7 kPa, purity >99.99%). The photocatalyst was placed in a U-shaped quartz reactor and irradiated with ultraviolet– visible (UV–Vis) light from a 300 W Xe arc lamp (Model MAX 350, Asahi Spectra, Japan) via a quartz light guide (diameter: 5 mm).⁵²⁵ The distance between the fiber light exit and the photocatalyst was maintained at 2 cm. The light intensity at the center of the sample was adjusted between 110 and 472 mW cm⁻² (Table 1a–d', main text). CO₂ photoreduction tests were also performed by cooling the quartz reactor with 2.5 L water in quartz bath (Chart S1).



Chart S1 A picture of CO_2 photoreduction test by cooling the quartz reactor with 2.5 L water in quartz bath.

Online gas chromatography–mass spectrometry (GC–MS) analysis was performed using a JMS-Q1050GC (JEOL, Japan). A packed column of 13X-S molecular sieves (length: 3 m, internal diameter: 3 mm; GL Sciences, Inc., Japan) was used, with He (purity >99.99995%) as the carrier gas. The ionization energy of the separated gas was 20 eV. Detection of ¹³CH₄ and ¹²CH₄ relied was based on their mass-to-charge ratios (m/z): ¹³CH₄ at m/z = 17 and ¹²CH₄ at m/z = 16. The fragment ratio of CH₃⁺: CH₄⁺ was 0.708:1. Similarly, ¹³CO was identified at m/z = 29, ¹³C₂H₆ and ¹³C₂H₄ at m/z = 30 as ¹³C₂H₄ fragment, ¹³C₃H₆ at m/z = 31 as ¹³C₂H₅⁺ fragment, and ¹³C₃H₆ at m/z = 44 as ¹³C₃H₅⁺ fragment. All reactants and products were uniquely quantified based on their GC retention times in the mass chromatogram.

 CO_2 photoconversion tests were conducted using CO_2 (95 kPa) and H_2O (70 mL) with NaHCO_3 (0.203 g, purity >99.5%; Wako Pure Chemical, Japan) dissolved in the solution. Photocatalyst samples

(2.7 mg), pretreated under H₂ were sealed by flame and transferred to a Pyrex flask reactor under an Ar atmosphere using the Schlenk technique. CO₂ (95 kPa) was circulated within a closed Pyrex glass system connected to the Pyrex flask, which was equipped with a quartz window containing the photocatalyst. The reactor was irradiated with UV–Vis light from a Model MAX-350 through a quartz light guide. The distance between the fiber light exit and the quartz window was 2 cm. The integrated light intensity for the suspended sample was measured at 367 mW per flask (Table 1e and e'). The suspension was stirred at 1,000 rpm, and the reaction gas was continuously bubbled using a gas circulation pump connected to the reactor during the photocatalytic reaction tests. Product analysis was performed using an online GC-thermal conductivity detector (Model GC-8AT, Shimadzu, Kyoto, Japan) equipped with a packed column of 13X-S molecular sieves (length: 3 m, internal diameter: 3 mm). Additionally, GC–MS analysis was conducted using a packed column of 13X-S molecular sieves, with He (purity >99.99995%) as the carrier gas in both cases.

UV-Vis spectra were recorded using a double-beam V-650 spectrometer (JASCO, Tokyo, Japan) equipped with D₂ and halogen lamps for measurements below and above 340 nm, respectively. A photomultiplier tube and an integrated ISV-469 sphere were used for diffuse reflectance detection in the 200-800 nm range. Samples pretreated under H₂ were transferred to an airtight cell using a vacuum-type glove box (UN-6509LCIY, Unico, Japan) under an Ar atmosphere. A polytetrafluoroethylene plate was used as the reference. Absorption and fluorescence spectra were recorded using an FP-8600 spectrometer (JASCO; Chiba lodine Resource Innovation Center, Chiba University, Japan) equipped with a 150 W Xe arc lamp (Type UXL-159, Ushio, Japan) and a photomultiplier tube. Excitation was performed at 200 nm, and fluorescence emission was measured in the 300-800 nm range. The incident excitation light from the Xe lamp was monitored using a Si photodiode, and the detected fluorescence was normalized based on the incident light intensity at each wavelength. The photocatalyst powder (2.0 mg) was dispersed in deionized water (< 0.055 μS cm^-1; 3.0 mL) and ultrasonicated (430 W, 38 kHz) for 30 min. All spectra were recorded for the suspensions in a quartz cell at 295 K.

Fe K-edge X-ray absorption fine structure spectra were measured at beamline 9C of the Photon Factory, High Energy Accelerator Research Organization, Tsukuba, Japan. A Si (1 1 1) double-crystal monochromator was used to analyze X-rays emitted from the storage ring via a bending magnet. The monochromator was adjusted using a piezo transducer and focused using a bent cylindrical mirror coated with Rh. Photocatalyst samples were pretreated in a quartz U-tube and transferred to a Pyrex cell filled with reaction gas ($CO_2 + H_2$). The cell was equipped with polyethylene terephthalate film (Toyobo, Japan, Type G2, 50 µm thick) on both sides. A 300 W Xe arc lamp (Model MAX 350) served as the light source, with a fiber light exit positioned 3 cm from the photocatalyst (322 mW cm⁻²).

X-ray diffraction patterns were recorded using a D8 ADVANCE diffractometer (Bruker, Billerica, MA, USA) at the Center for Analytical Instrumentation, Chiba University. The measurements

ChemComm

were conducted over a Bragg angle range of $2\theta_B = 10^\circ - 80^\circ$, with a scan step of 0.02° and a scan rate of 0.5 s per step. The instrument operated at 40 kV and 40 mA, utilizing Cu K α radiation (λ = 0.15419 nm) with a Ni filter.

In situ FTIR spectroscopy measurements were conducted at 295 K using a model FT/IR-4200 spectrometer (JASCO, Tokyo, Japan) over a spectral range of 4000–650 $cm^{-1}.$ The Fe (7.5 wt%)–ZrO_2 photocatalyst disk (60 mg), mixed with an equal amount of ZrO₂ (60 mg), was pretreated under H₂ at 973 K in a quartz cell and subsequently transferred to an FTIR cell under an Ar atmosphere using a vacuum-type glove box (UN-6509LCIY). A mixed gas of ¹³CO₂ (2.3 kPa) and H₂ (21.7 kPa) was introduced to the photocatalyst disk. The sample was then irradiated with UV-Vis light from a 300 W Xe arc lamp (Model MAX 350) via a quartz fiber light guide. Finally, the FTIR cell containing the photocatalyst disk was evacuated using rotary and diffusion pumps (10⁻⁶ Pa). The fiber light exit was positioned 3 cm from the sample disk, with an incident light intensity of 265 mW cm⁻². The spectrometer was set to an energy resolution of 1 cm⁻¹, and data accumulation was performed over 512 scans (~2 s per scan).

Spin-polarized periodic density functional (DFT) theory calculations were performed using the Vienna Ab initio Simulation Package code version 6.4.2^{\$26} on a WJ9J-W231 server equipped with an Intel Xeon w9-3495X processor (1.9 GHz, 56 cores; Tsukumo, Japan). Additionally, part of the computations was conducted using the supercomputer facilities at the Institute for Solid State Physics, University of Tokyo, Japan. The projector-augmented wave method was applied at the DFT-D3 level to account for van der Waals interactions. The generalized gradient approximation-revised Perdew–Burke–Ernzerhof exchange-correlation functional was utilized, with a plane-wave energy cutoff set at 500 eV.

The convergence criterion was set at 10^{-4} eV for the self-consistent field cycle, and structural optimizations were considered converged when the forces on all atoms were smaller than 1.0 eV nm⁻¹. All atoms were fully relaxed during structural optimization. The Brillouin zone was sampled using a $3 \times 3 \times 1$ wave number vector *k*-point grid. The (1 1 1) surface of body-centered cubic Fe was modeled using a $3 \times 3 \times 2$ unit cell slab, with a vacuum spacing of 1.5 nm between slabs.⁵²⁷

The adsorption energy (E_{ads}) of CO₂ was calculated based on eq. S1. $E_{ads} = E_{mol/slab} - E_{mol} - E_{slab}$, (S1)

where $E_{mol/slab}$ is the total energy of the adsorbate on the slab surface, and E_{mol} and E_{slab} are the energies of an isolated molecule in the gas phase and of the surface, respectively.

3. Results and discussion

3-1. Photocatalytic CO₂ reduction tests

The ¹³CO formation rate using Fe (7.5 wt%)–ZrO₂-973R photocatalyst @110 mW cm⁻² until 5 h of photoreaction under ¹³CO₂ (2.3 kPa) and H₂ (21.7 kPa; 3.7 μ mol h⁻¹ g_{cat}⁻¹; Table 1a) corresponds 0.37 μ mol of ¹³CO at 5 h. This exceeds the evaluated surface O vacancies (V₀^{••})

population: 0.070 μ mol per 20 mg of photocatalyst (Table S3g and Fig. S7), and suggests that ¹³CO was photocatalytically formed rather than stoichiometric reaction of CO₂ and V₀^{••} to form CO filling in the O vacancy.

A photocatalytic reduction test of CO₂ was performed in comparison to tests listed in Table 1 to verify H₂ pressure dependence. ¹³CO₂: H₂ ratio was 1: 9.4 in Table 1 while CO₂ (or CO): H₂ ratio was 1: (1–6) in tests in Table S4, except for reference S40. Therefore, a test at ¹³CO₂: H₂ ratio of 1: 1 was performed irradiated by light at 473 mW cm⁻² (Table S2b and b'). In comparison to the test using ¹³CO₂ and H₂ with the ratio 1: 9.4 (entries c and c'), the formation rate of ¹³CO₂ was suppressed to 40% while that of ¹³CH₄ became 1.0% of rates under higher H₂ pressure. Thus, H₂ pressure dependence suppressed the progress of sequential reaction steps from CO₂ to CO then CH₄ (Scheme 1a).

Next, a reference photocatalytic test was also performed using ZrO₂ reduced at 973 K under H₂ (Table S2a). The ¹³CO formation rate (1.7 μ mol h⁻¹ g_{cat}⁻¹) was significantly lower compared to initial ¹³CH₄ formation rate under similar photocatalytic reaction conditions (Table 1b). Furthermore, no trend was found between reduction temperature of photocatalyst under H₂ and the amount of chemisorbed CO₂ (Table S3), corresponding to O vacancy on the ZrO₂ surface. Thus, noncatalytic CO₂ reduction to CO by the reaction of V₀^{••} on ZrO₂ created by reduction at high temperature under H₂ was minimal in this study.

In the photocatalytic test using CO_2 and H_2O (Fig. S1), sequential trend of primary water photosplitting was observed as the quick O_2 evolution and secondary CO then CH_4 generation. This trend suggested the inclusion of reverse water–gas shift reaction step (eq. S3).

$$2H_2O \rightarrow 2H_2 + O_2$$
(S2)

$$CO_2 + H_2 \rightarrow CO + H_2O$$
(S3)

$$CO + 3H_2 \rightarrow CH_4 + H_2O$$
(S4)



Fig. S1 Time course of CO, CH₄, and O₂ formation using Fe⁰ (7.5 wt%)–ZrO₂-973R photocatalyst, with CO₂ (95 kPa), H₂O (70 mL), and UV–Vis light irradiation at 367 mW per cell. The O₂ amount was corrected by subtracting the N₂ amount multiplied by 20.9/78.1 at each time.

				Light	Stage of	Formation rate (μ mol h ⁻¹ g _{cat} ⁻¹)				
Entry	y Catalyst ¹³ CO ₂ H ₂ intensity (mW cm ⁻²)		reaction test (h)	¹³ CO	¹³ CH ₄	$^{13}C_{2}H_{6}$	$^{13}C_{3}H_{8}$	O ₂		
а	ZrO ₂	21.7 kPa		257	0–48	1.7	<0.002	<0.002	<0.002	
b		-e (7.5 %)–ZrO ₂ 2.3 kPa	2.3 kPa	473	0–5	27.7	1.75	0.0511	<0.002 <0.00	<0.002
b'	Fe (7.5				5–48	13.4	0.213	0.0302		
С	wt%)–ZrO ₂			472	0–5	69	170	2.1		
c'			ZI./ KPd	472	5-48	18	20	2.3	0.56	

Table S2 CO₂ photoreduction outcomes using ZrO₂ and Fe (7.5 wt%)–ZrO₂ both prereduced at 973 K in the presence of H₂.

Entries c and c' are the same as Table 1c and c' for comparison to entries b and b'.

Table S3 Chemisorbed amount of CO₂ during the photoexchange using ZrO_2 , Ag (5.0 wt%)– ZrO_2 , Au (5.0 wt%)– ZrO_2 , Ni (10 wt%)– ZrO_2 , Co (7.5 wt%)– ZrO_2 , and Fe (7.5 wt%)– ZrO_2 under UV–visible light irradiation

	¹³ CO ₂ (kPa)	Catalyst		Poduction tomposturo	Chamisarhad CO.	Reference
Entry		Туре	Amount (mg)	(K)	(μmol)	
а		ZrO ₂	100	-	2.3	S45
b		ZrO ₂	20	723	0.66	S46
С	0.67	Ag (5.0 wt%)–ZrO ₂	100	-	3.5	S45
d		Au (5.0 wt%)–ZrO ₂	100	-	2.9	S47
e		Ni (10 wt%)–ZrO ₂		723	0.54	S46
f	0.68	Co (7.5 wt%)–ZrO ₂	20	823	0.050	S25
g	0.69	Fe (7.5 wt%)–ZrO ₂]	973	0.070	This work

Table S4 Reported thermal catalysts that utilize Fe as active sites for CO₂ and/or CO hydrogenation into hydrocarbon(s).

Entry	Catalyst	T _{reduction} (K)	Fe state	T _{reaction} (K)	Reactant	Product	Formation rate	Ref.
а	Fe–CeO ₂	673	Fe ²⁺ , Fe ³⁺	623			26 mmol h ⁻¹ g _{Fe} ⁻¹	S29
b	$Fe-Ce_{0.1}Zr_{0.9}O_2$	573 (Ar)		573–773				S30
с	Fe–SiO ₂	623	γ -Fe ₂ O ₃	673			0.97 mol h ⁻¹ mol _{Fe} ⁻¹	S31
d	Fe-CeO ₂ -Al ₂ O ₃	1023	Fe, Fe ₂ O ₃ and Fe ₃ O ₄	683		CH4	6.2 mmol $h^{-1} g_{cat}^{-1}$	S32
е	Fe-mesoporous SiO ₂	623	Fe ³⁺	773			0.99 mmol h ⁻¹ g _{cat} ⁻¹	S33
f	Fe-mesoporous SiO ₂	773		623			35 mol h ⁻¹ mol _{Fe} ⁻¹	S34
g	Fe ^{II} (Fe ^{III} _{0.5} Al _{0.5}) ₂ O ₄		Fe₅C₂, Fe⁊C₃, Fe oxide	593	CO ₂		2.6 μ mol h ⁻¹ g _{cat} ⁻¹	S35
h	Fe–Al ₂ O ₃		Fo² + Fo³ +	673		C ₁₋₁₂ HC	0.14 mol h ⁻¹ g _{Fe} ⁻¹	S36
n	Fe–C		re-', re-'				0.068 mol h ⁻¹ g _{Fe} ⁻¹	
:			Fe_5C_2 , Fe_7C_3 ,	F03		CH ₄	46 mmol h ⁻¹ g _{cat} ⁻¹	627
1	Fe (Fe ^m 0.5Al0.5/2U4		Fe oxide	593		C ₂₋₄ HC	62 mmol h ⁻¹ g _{cat} ⁻¹	557
j	$Fe(Fe_{0.5}AI_{0.5})_2O_4$		Fe₅C₂, Fe⁊C₃, Fe oxide	593			46 mmol h ⁻¹ g _{cat} ⁻¹	S38
Ŀ				623		<u>cu</u>	0.52 mmol h ⁻¹ g _{Fe} ⁻¹	620
к	k Fe–SiO ₂			663		CH_4	1.4 mmol h ⁻¹ g _{Fe} ⁻¹	239
Ι	Blast furnace sludge (Fe rich)	773	Fe ₂ O ₃ , Fe ₃ O ₄	593	60		0.16 mmol h ⁻¹ g _{cat} ⁻¹	S40
m	Fe–Zn oxide	613 (Ar)	Fe_2C , Fe_5C_2	613			5.0 mol h ⁻¹ g _{Fe} ⁻¹	S41
	Fa C	none		F 49		C ₁₋₅ HC	2.5 mmol h ⁻¹ g _{cat} ⁻¹	S42
n	re-L	673		548			4.1 mmol h ⁻¹ g _{cat} ⁻¹	

ChemComm

3-2. Charactrizations



Fig. S2 Diffuse-reflectance UV–Vis absorption spectra for (a) ZrO_2 , (b) incipient Fe₃O₄– ZrO_2 , (c) Fe⁰ (7.5 wt%)– ZrO_2 -973R, and (d) Fe⁰ (7.5 wt%)– ZrO_2 -973R after a 48-h photocatalytic ¹³CO₂ reduction test.



Fig. S3 Normalized Fe K-edge X-ray absorption near-edge structures for (A) (a) incipient Fe_3O_4 –Zr O_2 , (b) Fe^0 (5.0 wt%)–Zr O_2 reduced at 973 K, (c) standard Fe⁰ metal, and (d) Fe_3O_4 ;⁵²⁸ and (B) (a) Fe⁰ (7.5 wt%)–Zr O_2 -973R under CO₂ (2.3 kPa) and H₂ (21.7 kPa) in the dark, (b) standard Fe⁰ metal, (c) FeO, and (d) the convolution spectrum of Fe⁰ metal and FeO with a mixing ratio of 8: 2.



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Fig. S4 Fourier transform of angular wave number k^3 -weighted Fe K-edge extended X-ray absorption fine structure measured for (a) Fe⁰ (5.0 wt%)–ZrO₂ and (b) Fe⁰ (20 wt%)–ZrO₂, both reduced under H₂ at 973 K, and (c) Fe⁰ foil (thickness 4 µm).



Fig. S5 X-ray diffraction pattern for (a) Fe^0 (7.5 wt%)–ZrO₂-973R and (b) Fe^0 (7.5 wt%)–ZrO₂-973R after a 48-h photocatalytic ¹³CO₂ reduction test.

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Interband emission peaks may be owing to elemental impurity energy level⁵⁴³ as well as impurity energy level (Fig. S6; see main text). The major impurity in ZrO_2 employed was HfO₂: Hf/(Zr + Hf) ratio was 0.77 wt% (see the Experimental section). A part of the peak at 468 nm in Fig. S6 may be owing to HfO₂.⁵⁴⁴

The ¹³CO₂ exchange test using Fe⁰ (7.5 wt%)–ZrO₂ showed quick adsorption of ¹³CO₂ (99%) and ¹²CO₂ (1%) (in total 20 µmol) followed by gas temperature increase (gas expansion) simulated by sigmoid function as well as slower adsorption of CO₂ (in total 4.1 µmol). The remaining term of relatively quick ¹²CO₂ increase (0.070 µmol; Table S3g and Fig. S7) suggested preadsorbed ¹²CO₂ on V₀^{••} site.^{525,545–547} Based on this amount, surface V₀^{••} sites were evaluated to one per 44 nm² (see main text).



Fig. S6 UV–Vis fluorescence emission spectra for (a) ZrO_2 , (b) incipient Fe_3O_4 – ZrO_2 , and (c) Fe^0 (7.5 wt%)– ZrO_2 -973R at an excitation wavelength of 200 nm.



Fig. S7 Time course of ¹³CO₂ (0.69 kPa) exchange reaction using Fe⁰ (7.5 wt%)–ZrO₂-973R (20 mg) irradiated by UV–visible light (270 mW cm⁻²). Temperature change upon light irradiation was simulated by sigmoid function.



Fig. S8 FTIR spectra for Fe⁰ (7.5 wt%)–ZrO₂-973R under 13 CO₂ (2.3 kPa) and H₂ (21.7 kPa) (a) and during UV–Vis light irradiation (265 mW cm⁻²; (b)).

Author contributions

TO and IA did experiments and analyzed while MS did theoretical calculations. YI made plan and wrote paper.

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ChemComm

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