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

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Selective photoreduction of CO₂ to CO, CH₄, and C_{2–3} paraffins was directed by increasing ultraviolet-visible light intensity over an Fe–ZrO₂ photocatalyst. Fe⁰ nanoparticles sequentially reduced COH—transferred from the ZrO₂ surface—into CH_x species and hydrocarbons, facilitated by light-induced heating to ~452 K.

Photocatalytic CO₂ reduction establishes a novel C-neutral cycle and is considered a potential environmental solution for a sustainable society.^{1,2} However, its near-term implementation is hindered by economic challenges, primarily due to the costs of photocatalysts and reactor design.^{3,4} Among first-row transition metals, Fe is the most abundant and cost-effective. Consequently, Fe-based photocatalysts for CO₂ photoreduction have been widely studied. However, nearly all reported systems employ Fe in the form of metal ions within metal-organic frameworks, covalent organic frameworks, porphyrins, or as Fe₂O₃, functioning primarily as redox mediators (Table S1, ESI†).⁵

In this study, a Fe⁰ surface was evaluated as a CO₂ photoreduction catalyst for C_{1–3} hydrocarbons (HCs) in combination with semiconductor ZrO₂. An Fe₃O₄–ZrO₂ composite was synthesized *via* a liquid-phase reduction method, using Fe(NO₃)₃·9H₂O as the precursor and reducing it at 973 K under H₂ to obtain the Fe⁰ (7.5 wt%)–ZrO₂-973R photocatalyst. The valence state and coordination of Fe were monitored during synthesis using X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS).

This approach facilitated the formation of bifunctional sites—O vacancies (V_O[•]) on the ZrO₂ surface^{3,6–9} and Fe⁰ nanoparticles—enabling the selective photogeneration of CO and C_{1–3} HCs from CO₂. At a ultraviolet-visible (UV-Vis) light intensity of 110 mW cm^{−2}, using ¹³CO₂ and H₂ gases with the Fe⁰ (7.5 wt%)–ZrO₂-973R photocatalyst, both ¹³CO and ¹³CH₄

were gradually generated over the first 5 h of photoreaction (Table 1a). However, beyond this period, ¹³CO formation became predominant (>99 mol% selectivity; entry a'), as subsequent reaction steps from CO did not proceed (Scheme 1a). The steady photogeneration of CO was significantly faster than that observed with ZrO₂ alone (Table S2a, ESI†),^{6–8} confirming the active role of the Fe⁰ surface, but the selectivity change after 5 h seemed due to strong CO₂ adsorption on it in CO₂ photoreduction (see below).

In stark contrast, increasing the irradiated light intensity to 322 mW cm^{−2} shifted the Fe⁰–ZrO₂-973R photocatalyst from selective two-electron reduction to ¹³CO to predominant eight-electron reduction to ¹³CH₄ production (>95 mol% selectivity; Table 1b). This shift occurred because the hydrogenation steps from CO proceeded rapidly under higher light intensity, facilitating the sequential reduction from CO₂ to CO and ultimately to CH₄. From a practical perspective, however, the ¹³CH₄ light-induced synthesis using Fe⁰–ZrO₂ requires further improvement, as photocatalytic activity declined after 5 h of photoreaction—more so than under 110 mW cm^{−2} irradiation (Table 1a' and b'). As no CH_x species were observed in the Fourier transform infrared (FTIR) spectrum under the conditions, this deactivation was attributed to Fe⁰ surface poisoning by strongly adsorbed CO₂ (Scheme 1b).

To enhance the stability of the Fe⁰–ZrO₂-973R photocatalyst, the irradiated light intensity was further increased to 472 mW cm^{−2}. Under these conditions, the ¹³CH₄ formation rate reached 170 μmol h^{−1} g_{cat}^{−1} with >71 mol% selectivity, accompanied by ¹³CO formation at 69 μmol h^{−1} g_{cat}^{−1} (>28 mol% selectivity) over 5 h of photoreaction (Fig. 1A and Table 1c). Over time, ¹³CH₄ formation exhibited a turning point at ~5 h of photoreaction (Fig. 1A), attributed to partial Fe⁰ site poisoning by intermediate species such as HCO₂ and CH_x. Beyond this period, the ¹³CH₄ formation rate stabilized at 20 μmol h^{−1} g_{cat}^{−1} with >49 mol% selectivity (Table 1c' and Scheme 1c). Under the steady conditions, CO₂ blocking on Fe⁰ sites should be less effective in contrast to the status under 110–322 mW cm^{−2} irradiation. This time-dependent product distribution confirmed a consecutive

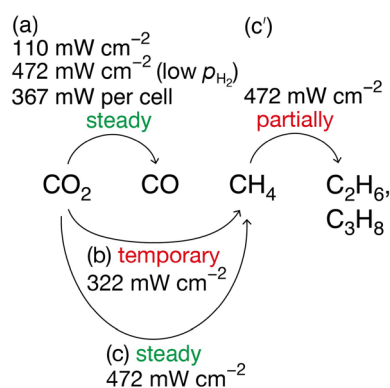
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† Electronic supplementary information (ESI) available: Lists of reported photo- and thermal catalysts, experimental details, photocatalytic time course, X-ray diffraction, and optical, X-ray absorption, and FTIR spectroscopy of photocatalyst and surface species. See DOI: <https://doi.org/10.1039/d5cc01147g>



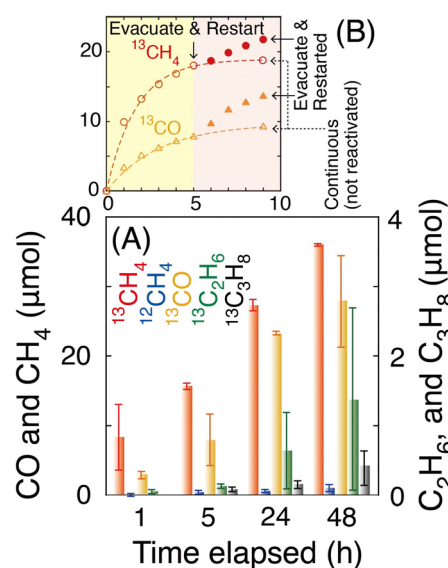
Table 1 CO₂ photoreduction outcomes using Fe (7.5 wt%)-ZrO₂ prereduced at 973 K in the presence of either H₂ or H₂O

Entry	Reactant	Reductant	Light intensity (mW)	Stage of reaction test (h)	Formation rate (μmol h ⁻¹ g _{cat} ⁻¹)				
					¹³ CO	¹³ CH ₄	¹³ C ₂ H ₆	¹³ C ₃ H ₈	O ₂
a	¹³ CO ₂ (2.3 kPa)	H ₂ (21.7 kPa)	110 cm ⁻²	0–5	3.7	3.8	0.052	0.018	< 0.002
a'				5–48	3.7	< 0.002	< 0.002	< 0.002	
b			322 cm ⁻²	0–5	2.4	45	0.20		
b'				5–48	1.7	1.1	0.036		
c			472 cm ⁻²	0–5	69	170	2.1	0.30	
c'				5–48	18	20	2.3	0.56	
c''				(20–48)	(2.7)	(16)	(2.6)	(0.70)	
d			1510 cm ⁻²	0–5	35	40	0.26	< 0.002	< 0.002
d'			(with water bath)	5–48	5.2	0.41	0.037		
e	CO ₂ (95 kPa)	H ₂ O (70 mL)	367 per cell	0–5	CO	CH ₄	C ₂ H ₆	C ₃ H ₈	O ₂
e'				5–48	12	< 0.002	< 0.002		64
					8.5	0.86			9.0

**Scheme 1** Temporary and steady CO₂ photoreduction pathways directed by irradiated light intensity (110–472 mW cm⁻²) using the Fe⁰ (7.5 wt%)-ZrO₂-973R photocatalyst in presence of H₂ ((a)–(c) and (c')) or H₂O (a).

reaction pathway: CO₂ reduction to CO, followed by CH₄ formation, and subsequent conversion to C_{2,3} hydrocarbons. Between 20 and 48 h of photoreaction, the ¹³CH₄ formation rate remained stable (> 73 mol% selectivity), while ¹³C₂H₆ and ¹³C₃H₈ selectivity significantly increased to 15 mol% (total formation rate: 3.3 μmol h⁻¹ g_{cat}⁻¹), effectively suppressing initial ¹³CO production (Table 1c'' and Scheme 1c'). Notably, no C₂H₄ or C₃H₆ was detected. Furthermore, photocatalytic activity could be restored by a 1-h evacuation at 10⁻⁶ Pa under light, reactivating the consecutive reduction process from CO to CH₄ (Fig. 1B).

The other photocatalytic test was using CO₂ (2.3 kPa), H₂ (21.7 kPa), and the light irradiation at 1510 mW cm⁻², but the quartz reactor was cooled with water bath (Table 1d–d' and Chart S1, ESI†). The ¹³CO and ¹³CH₄ formation rates were 24–51% of corresponding rates without water cooling until 5 h of reaction (Table 1c and c'), while the decline after 5 h was more significant, especially for ¹³CH₄ formation, strongly suggesting that charge separation in/on ZrO₂ owing to light proceeded CO₂ reduction while Fe nanoparticle surface at lower temperature in thermal equilibrium with ZrO₂, reactor, and 2.5 L of water was deactivated for subsequent multiple hydrogenation earlier by adsorbed species, e.g. CO₂. The increase of water temperature was minimal: from 295.2 to 295.5 K during the photocatalytic test for 48 h (Chart S1, ESI†).

**Fig. 1** (A) and (B) Time course of ¹³CO, ¹³CH₄, ¹²CH₄, ¹³C₂H₆, and ¹³C₃H₈ formation using Fe⁰ (7.5 wt%)-ZrO₂-973R, ¹³CO₂ (2.3 kPa), H₂ (21.7 kPa), and UV-Vis light irradiation at 472 mW cm⁻². (B) Comparison with the reactivation test (filled symbols) after 1 h of catalyst evacuation under UV-Vis light irradiation at the 5-h mark.

Steady photocatalytic CO₂ reduction was also achieved using H₂O as the reductant instead of H₂ under UV-Vis light irradiation at 367 mW per cell. CO was continuously generated at a rate of 12–8.5 μmol h⁻¹ g_{cat}⁻¹ (Table 1e and e'), proceeding more rapidly than the multiple hydrogenation steps required for CH₄ formation over Fe⁰ (selectivity < 9.2 mol%; Scheme 1a and Fig. S1, ESI†). This was attributed to the predominant presence of H₂O rather than H at the Fe⁰ surface, which favored CO generation over further hydrogenation to CH₄.

The effects of UV-Vis light irradiation on the Fe⁰-ZrO₂-973R photocatalyst were investigated. In the UV-Vis absorption spectra of the Fe₃O₄-ZrO₂ sample (Fig. S2b, ESI†), two absorption shoulders at 410 and 525 nm, attributed to Fe²⁺ and Fe³⁺ ions, were observed, whereas ZrO₂ alone exhibited no visible light absorption (spectrum a). This spectral profile was consistent with the reported absorption spectrum of Fe₃O₄.¹⁰ Upon H₂ treatment at 973 K, absorption extended across the entire visible region



(spectrum c), and the spectrum remained similar after 48 h of photocatalytic $^{13}\text{CO}_2$ reduction (spectrum d), confirming the formation and stability of Fe^0 nanoparticles, which facilitated multiple hydrogenation steps from CO/COH species (Scheme 1c and c'). The Fe valence state assignments were corroborated by changes in the XANES spectrum, aligning with those of standard Fe^0 and Fe_3O_4 (Fig. S3A(c) and (d), ESI†).¹¹ EXAFS Fourier transform analysis of Fe^0 -ZrO₂-973R revealed interatomic pairs characteristic of Fe^0 (Fig. S4, ESI†), while X-ray diffraction showed an Fe (011) peak overlapping with peaks corresponding to monoclinic ZrO₂ (Fig. S5, ESI†), further supporting the formation of Fe^0 active sites in the Fe^0 -ZrO₂-973R photocatalyst.

The fluorescence emission spectra of Fe^0 -ZrO₂-973R were measured under excitation at 200 nm (Fig. S6, ESI†), a wavelength corresponding to an energy higher than the band gap of ZrO₂ (Fig. S2a, ESI†). The spectrum exhibited both an interband excitation–deexcitation peak centered at 367 nm (spectrum a) and intraband transition peaks associated with impurity levels, such as O vacancies and Hf (0.55 wt%) in/on ZrO₂, appearing at 451, 468, 481, 491, 528, and 623 nm. These emissions were significantly suppressed upon the addition of Fe_3O_4 and further reduced with Fe^0 nanoparticles (spectra b and c), indicating effective trapping of excited electrons at the conduction band (CB) of ZrO₂.

Next, the reaction pathway from CO₂ to CO and HCs is considered. The role of $\text{V}_\text{O}^\bullet$ sites on the ZrO₂ surface in CO₂ adsorption and its subsequent photoreduction to OCOH and COH species was analyzed using density functional theory (DFT) calculations.⁹ The population of surface $\text{V}_\text{O}^\bullet$ sites was evaluated to one per 44 nm² based on $^{13}\text{CO}_2$ exchange amount with preadsorbed $^{12}\text{CO}_2$ on $\text{V}_\text{O}^\bullet$ site (0.070 μmol ; Table S3g and Fig. S7, ESI†). The population of surface $\text{V}_\text{O}^\bullet$ sites seems not vary much before and after photocatalytic test based on essentially negligibly-changing UV-visible and XRD data (Fig. S2c, d and S5a, b, ESI†). Consequently, this study focuses on the critical steps enabling transient or sustained C_{1–3} photogeneration (Scheme 1b and c), specifically the conversion of COH and/or CO into C_{1–3} HCs over the Fe^0 surface.

To identify the active sites responsible for these reaction steps, Fe K-edge EXAFS measurements were conducted on the Fe^0 -ZrO₂-973R photocatalyst under CO₂ and H₂ exposure. Unexpectedly, ~20% of the Fe^0 sites reduced at 973 K were oxidized upon reaction with CO₂ in the dark, as indicated by EXAFS analysis (Fig. 2A, 0 min). The spectral fit, obtained by convolving standard XANES spectra for Fe^0 and FeO with an 8:2 mixing ratio (Fig. S3B(d), ESI†), aligned with the EXAFS data. This oxidation is attributed to the formation of an M-shaped $\text{Fe}^{2+}\text{-O-C(=Fe}^0\text{)-O-Fe}^{2+}$ species upon CO₂ adsorption on Fe. DFT calculations further support the energetic stability of this species on the Fe^0 (111) surface, with an adsorption energy of 0.92 eV and a Bader charge of +0.352 on Fe bonded to O, consistent with prior studies.¹² At this stage, CO did not desorb spontaneously from Fe surface and was not detected.

Upon UV-Vis light irradiation, the Fourier transform of EXAFS spectra (Fig. 2A, 0 min) showed that the Fe–O and Fe···Fe peaks corresponding to FeO were rapidly replaced by

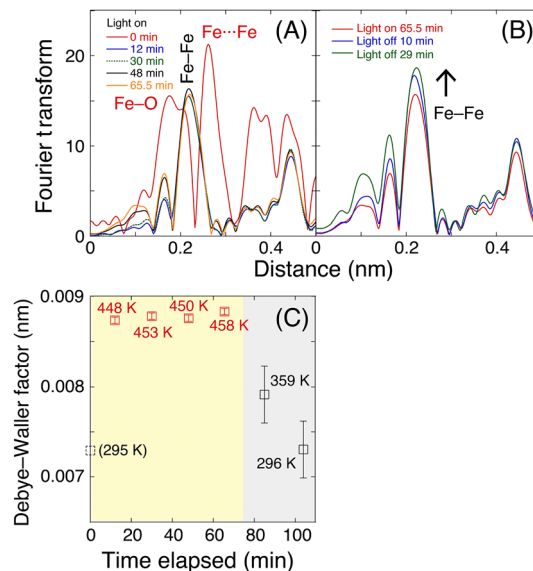


Fig. 2 Time-dependent Fourier transform of Fe K-edge EXAFS for Fe^0 (7.5 wt%)-ZrO₂-973R under CO₂ (2.3 kPa), H₂ (21.7 kPa), and UV-Vis light irradiation (322 mW cm^{−2}). (A) During 75 min of illumination, (B) after the light was turned off, and (C) corresponding time-dependent evolution of the Debye–Waller factor for the Fe–Fe interatomic pair.

a metallic Fe–Fe peak at 0.21 nm (phase shift uncorrected; Fig. 2A, 12 min). This transformation indicates the reduction of Fe^{2+} in the M-shaped $\text{Fe}^{2+}\text{-O-C(=Fe}^0\text{)-O-Fe}^{2+}$ species.

In the FTIR spectrum of Fe^0 -ZrO₂-973R under $^{13}\text{CO}_2$ and H₂ (Fig. S8, ESI†), shoulder peaks at 1584, 1396, and 1217 cm^{−1} corresponded to $\nu_{\text{as}}(\text{OCO})$, $\nu_{\text{s}}(\text{OCO})$, and $\delta(\text{OH})$ bending vibrations, respectively, were attributed to monodentate and bridging bicarbonate species adsorbed on the surface.^{6–8} In contrast, the broader peaks centered at 1538 and 1261 cm^{−1} were tentatively assigned $\nu_{\text{as}}(\text{OCO})$ and $\nu_{\text{s}}(\text{OCO})$ stretching vibrations of bidentate carbonate species on ZrO₂,¹³ as well as the M-shaped $\text{Fe-O-C(=Fe}^0\text{)-O-Fe}$ species proposed earlier, adsorbed at various sites on the Fe^0 surface. This assignment aligns with DFT-calculated O–C–O bond angles of 122°. Upon UV-Vis light irradiation (265 mW cm^{−2}), the peak associated with $^{13}\text{CO}_2$ and H₂ adsorption negatively shifted by 41 cm^{−1}. This shift was attributed to the reduction of Fe^{2+} to Fe^0 via electron transfer from ZrO₂ CB to Fe, followed by electron injection into the σ^* orbitals of C–O bonds, facilitating bond weakening and activation under UV-Vis illumination, in consistent with the reduction from Fe^{2+} to Fe^0 upon the light irradiation based on EXAFS (Fig. 2A).

The broad peak centered at 1497 cm^{−1} disappeared within 4 min under vacuum and UV-Vis light irradiation, likely due to CO₂ desorption, suggesting that CO₂ and carbonate species are not direct intermediates in C_{1–3} HC formation. In contrast, the conversion of adsorbed CO₂ on the ZrO₂ surface to COH species appears to be the rate-limiting step, as only methane (ν_3 peak at 3010 cm^{−1}) was detected alongside adsorbed CO₂ and bicarbonate species.

To elucidate the energetic origins of the multiple hydrogenation steps in which COH and/or CO species migrate over the Fe^0 surface to form HCs, the Fe–Fe coordination number was



determined *via* EXAFS as 5.3, corresponding to a surface dispersion of 0.95.¹⁴ In the correlated Debye model, the Debye temperatures of bulk and surface Fe (vertical motion) are reported as 467 K¹⁵ and 225 K,¹⁶ respectively. Using multiple scattering calculation code FEFF¹⁷ and plane-wave EXAFS analysis code XDAP,¹⁸ the local Fe site temperature during CO₂ photoreduction was experimentally monitored. Upon UV-Vis light irradiation, the Fe site temperature rapidly increased to ~452 (±35) K as hot spot due to light absorption and remained nearly constant at thermal equilibrium with the supporting ZrO₂ and the EXAFS cell both at ~295 K (Fig. 2C, left).

When the light was turned off, the heat generated by light energy dissipated, and the Fe site temperature returned to 296 K (Fig. 2C, right). This observation confirms that the selective formation of C_{1–3} HCs in this study resulted from a two-step process: (i) CO₂ reduction to COH/CO *via* charge separation in ZrO₂^{3,6–8} and (ii) subsequent multiple hydrogenation of CO/COH on the Fe⁰ surface, which was maintained at ~452 K due to light absorption.

Thermal CO₂ hydrogenation and Fischer-Tropsch synthesis of HC(s) using Fe-based catalysts typically require reaction temperatures above 548 K (Table S4, ESI†) to achieve HC formation rates comparable to the Fe site temperature (~452 K, Fig. 2C) and the observed rate of 0.24 mmol h^{–1} g_{cat}^{–1} (Table 1c) in this study. Under CO₂ photoreduction conditions, Fe sites remained exclusively in the Fe⁰ state (Fig. 2A and B), whereas thermal CO₂ reduction commonly involves Fe oxides and carbides (Table S4, ESI†). While the initial reduction of the first O atom in CO₂ over Fe⁰ surfaces¹⁹ typically requires high temperatures (>548 K),²⁰ this study demonstrates that the first reduction step was instead facilitated by charge separation at V_O^{••} sites on the ZrO₂ surface under light irradiation, enabling the reaction:



as previously reported.⁹ This step was particularly effective at lower light intensities (110–322 mW cm^{–2}; Table 1a–b') in the presence of neighboring Fe⁰ nanoparticles. The subsequent hydrogenation pathway, where COH migrates to Fe⁰ and undergoes further reduction to C_{1–3} HCs, is likely a common feature in both thermal (Table S4, ESI†) and photo (~452 K, Fig. 2C) reactions, regardless of whether H₂ or H₂O serves as the reductant.

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Data availability

The supporting data have been included as part of the ESI.†

Conflicts of interest

There are no conflicts to declare.

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