Supplementary Materials

Synthesis of Synergistic Catalysts: Integrating Defects, SMSI, and Plasmonic Effects for Enhanced Photocatalytic CO₂ Reduction

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EXPERIMENTAL

Synthesis of TiO₂-loaded Dendritic Fibrous Nanosilica (DFNS/TiO₂)

DFNS was synthesized using a previously reported protocol.¹ TiO₂ coating was achieved through ammonia-assisted solution-phase deposition. Initially, four separate 500 mL round bottom flasks, each containing 0.5 g × 4 of DFNS and 200 mL of ethanol, underwent 15 minutes of sonication to disperse the DFNS powder. Subsequently, the four suspensions were combined in a 2 L round bottom flask and stirred for 5 minutes at 24 °C with a rotation speed of 500 rpm. A 4 mL aqueous ammonia solution (25%) was then added dropwise over 5 minutes to attain a pH of 10. Following 5 minutes of stirring, the Ti precursor, titanium butoxide (TBOT, 10 mL), was added dropwise over approximately 10 minutes at 24 °C under continuous stirring. The solution temperature was then raised to 45 °C and maintained for 24 hours with continuous stirring. The resulting product was isolated by centrifugation (10000 rpm, 10 minutes), washed three times with ethanol, and dried at 80 °C in an oven for 6 hours. The isolated powder was subsequently heat-treated at 750 °C (with a ramp rate of 10 °C/min) in a muffle furnace for 5 hours in air.

Loading of Cu on DFNS/TiO₂

Cu nanoparticles were loaded on DFNS/TiO₂ by following a deposition-precipitation (DP) method. 100 mg of DFNS/TiO₂ was dispersed in 50 mL deionized water under continuous stirring followed by 2 minutes of sonication. he pH of the solution was adjusted to 10 by adding 30 μ L of NH₄OH solution. Desired quantities of the copper precursor (Cu(NO₃)·3H₂O) were dissolved in 2 mL of deionized water and then added dropwise into the DFNS/TiO₂-water suspension. The solution was stirred for 24 hours, and subsequently, the solvent was evaporated using a rotary evaporator at 45 °C. The resulting powder was labelled DFNS/TiO₂-Cux (ASP) (x = 0.05, 4, 10, and 20), where x denotes the weight percentage of copper content.

Catalyst Characterization

Scanning transmission electron microscopy (STEM) analysis was carried out using FEI-TITAN operated at an accelerating voltage of 300 kV. Elemental mapping was performed using energy-dispersive X-ray spectroscopy (EDS). A small amount of solid powder was dispersed in ethanol by sonicating for 30 seconds, and the dispersion was drop-casted onto a holey carbon-coated 200 mesh gold TEM grid. PXRD patterns were obtained using a PANalytical X'Pert Pro powder X-ray diffractometer with Cu-K radiation. A JASCO UV/vis/NIR spectrophotometer was used to conduct UV-Vis spectroscopic measurements. The baseline subtraction process was carried out (to reduce potential scattering effects) by first recording the UV-Vis diffuse reflectance spectra (DRS) of DFNS and then subtracting it from the UV-Vis DRS of DFNS/TiO₂ and DFNS/TiO₂-Cu catalysts. N₂ sorption measurements were performed using a Micromeritics 3-Flex surface analyzer (samples were degassed at 120 °C overnight under vacuum before analysis).

Photoluminescence (PL) spectra were recorded for DFNS/TiO₂, DFNS/TiO₂-Cu4 and DFNS/TiO₂-Cu10 catalyst using 320 nm diode laser for excitation in FluoroLog (Hori Jobin Yvon Inc.) spectrofluorometer.

XPS analysis was carried out using a Thermo K α + spectrometer with micro-focused and monochromated Al-K α radiation (1486.6 eV) as the X-ray source. The sample was prepared by sprinkling solid powder on carbon tape. The carbon signal at 284.8 eV was used as an internal reference.

X-ray absorption spectroscopy (XAS)

XAS analysis was performed at BL01B1 beamline in SPring-8. The incident X-ray beam for Cu-K edge XAS was obtained by using Si(111) double-crystal monochromator and Cu-K X-ray absorption near edge structure (XANES) spectra of reference samples and DFNS/TiO₂-Cu20 were recorded in transition mode using ionization chambers as detectors. In the case of DFNS/TiO₂-Cu0.05, XANES spectra were obtained in fluorescence mode using 19-element Ge solid state detector. To investigate the electronic states of catalysts under visible (\geq 420 nm) and UV (\geq 360 nm) lights, Cu-K edge XANES spectra were measured under the visible and UV irradiation using 300 W Xe ramp equipped with L420 and U360 cut-off filters. The data were analyzed by xTunes software.²

Temperature Programmed Reduction (H₂-TPR)

The H₂-TPR measurements were performed using a Catalyst Analyzer BELCAT II coupled with a Quadrupole mass spectrometer (Belmass). DFNS-TiO₂-Cu10 (ASP) (30 mg) sample was loaded into a quartz reactor and pretreated with a 20.0 vol.% O₂/Argon (Ar) mixture (30 mL min⁻¹) at 550 °C (ramp- 10 °C/min) for 2 h. After being cooled to room temperature (30 °C) under Ar flow (30 mL min⁻¹), the sample was exposed to a 5.0 vol.% H₂/Ar mixture (30 mL min⁻¹) and heated to 700 °C at a rate of 5 °C min⁻¹ and the mass detector signals for m/z=2 were analysed.

Photocatalytic CO₂ reduction to CO

Photocatalytic CO₂ reduction was carried out in a PIKE technologies flow reaction chamber with a quartz window equipped with a heater, an external thermocouple to precisely measure the temperature of the surface of catalyst bed, a thermocouple to measure reactor temperature further connected to a temperature controller (Scheme S1). The external thermocouple was The inlet of the flow reactor chamber was connected to mass flow controllers (MFCs), and the outlet was connected to an Agilent 490 MicroGC equipped with A CP-PoraPLOT U column and a thermal conductivity detector (TCD).

The catalyst DFNS/TiO₂-CuX (ASP) (5 mg) was taken in a ceramic porous base crucible, which was placed inside the reactor chamber. The catalyst was heated to 550°C in 70 mL min⁻¹ air flow (10 °C min⁻¹) for 2h. The temperature was increased to 650 °C (10 °C min⁻¹) in Ar flow of 50 mL min⁻¹ to flush the air out. After reaching 650 °C the flow was changed to H₂ (50 mL min⁻¹) and the sample was reduced for 4h. The catalyst was cooled to room temperature in argon gas (50 mL min⁻¹) and the reactant gases were then introduced into the reactor chamber through Alicat mass flow controllers; CO₂ at 80 mL min⁻¹, H₂ at 1 mL min⁻¹, Ar (20 mL min⁻¹) at 1 bar pressure. The catalyst was then irradiated with light (300 W Xenon Lamp ~5.1 W cm⁻², 230–1100 nm), and the progress of the reaction was monitored by using online MicroGC every 4 minutes. Higher temperature studies in the dark were performed by providing external heating to the catalyst bed by the heater inside the reaction chamber. For quantification, the GC was calibrated by injecting known concentrations of standard gases like H₂, O₂, N₂, CO₂, CH₄, C₂H₄, C₂H₆, C₂H₂, and higher hydrocarbons till C4. The slope of peak area versus ppm plot gives the calibration constant (area/ppm), which was used to calculate the product formation rate and selectivity of the products formed. Production rate, selectivity and apparent activation energy were calculated using the below formulae,

CO Production Rate (mmol
$$g_{cu}^{-1} h^{-1}$$
) = $\frac{(CO_{out} - CO_{in})(in ppm) \times Total flow(\frac{mL}{min}) \times 60}{Wt. of Cu in catalyst (in g) \times 22400 X 1000}$

CO Selectivity (%) =
$$\frac{CO Production Rate}{CO Production Rate + C_{\chi}H_{\chi}Production Rate}$$

$$E_a = -\frac{2.303 \, R \, dlog(R_{CO})}{d(1/T)} \, (\text{J mol}^{-1})$$

High-Energy-Resolution Fluorescence-Detection X-ray Absorption Spectroscopy Study

The High-Energy-Resolution Fluorescence-Detection X-ray Absorption Near Edge Spectroscopy (HERFD-XANES) spectra were obtained at the ID26 beamline of the European Synchrotron Radiation Facility (ESRF) in 16-bunch mode with a ring current of 75 mA. The incident energy was selected using the Si (111) reflection of a double crystal monochromator from the fundamental of three undulators with a 35 mm period and a length of 1.6 m. The beam size was approximately 0.2 x 0.1 mm² (horizontal x vertical) with a total flux of 10¹³ photons/second. The emission spectrometer was tuned to the maximum of the K α 1 lines of Ti and Cu using the Ge(400) and Si (444) reflections. All crystal analyzers were spherical, with a bending radius of 1 m and a diameter of 100 mm. The central crystal of the spectrometer was positioned at a scattering angle of 90 degrees. A Dectris Pilatus 100k detector was used for single photon counting. The incident beam energy was scanned with the Si (311) monochromator crystal at a fixed undulator gap, while the fluorescence detector's energy was fixed at the maximum energy of the Zn Kal emission line. Both in-situ and ex-situ HERFD-XANES measurements were performed at various temperatures using in-situ reactor cell available at the ESRF. The gas atmosphere in the reactor was controlled by three mass-flow controllers (Bronkhorst). XANES spectra were acquired with 10 consecutive scans, each lasting 60 seconds. Radiation damage was checked by comparing two consecutive scans, and no X-ray beam-induced spectral changes were observed. The energy range was 100 eV around the absorption edge, with an energy step size of 0.0001 keV, ensuring precise data acquisition and resolution. All spectra were normalized to the spectral area, and reference spectra were measured in the thick absorption limit and corrected for over-absorption effects.

The experimental procedure was conducted within a temperature range of 30°C to 650°C, and 1 bar pressure, with scans at 30°C, 140°C, 350°C, 550°C, and 650°C, employing a ramp rate of 8.5°C per minute. A continuous flow of 20 mL min⁻¹ of hydrogen gas was maintained to ensure a stable environment. *In-situ* XANES measurements were also performed to capture real-time changes in metallic and ceria sites during photocatalytic CO₂ reduction in the presence of reactant gases. The catalyst was irradiated with Xenon lamp from 230 nm to 1100 nm, at the intensity of 5.1 Wcm⁻² with scans in dark and light in different atmospheres, in the presence of only H₂, only CO₂, and H₂ + CO₂ gases (10 mL min⁻¹ each). To study the interaction of CO₂ with Cu and TiO₂ defect sites, *in-situ* XANES measurements were performed only in the presence of CO₂ flow (no hydrogen).

Electron Paramagnetic Resonance (EPR)

EPR spectra of all samples were recorded at room temperature in light (UV-Vis-IR) using JEOL EPR Spectrometer. 10 mg of the sample was used with the power of 5 mW, modulation frequency of 100 kHz taking 5 scans. The optimized flow conditions were used with CO_2 flow being 80 mL min⁻¹, H₂ being 1 mL min⁻¹ and Ar being 20 mL min⁻¹ and the spectra were recorded in light for inert (Ar) and reaction conditions.

Finite Difference Time Domain (FDTD) Simulations

The electric field enhancement calculations were performed by the finite difference time domain method. For simulation, the Cu NPs were modelled as spheres of 5 nm in diameter. We modelled 2 Cu NPs at a distance of 1.5 nm from each other. The Cu NPs were placed on a TiO₂ sheet of 5 nm thickness. This model was chosen to mimic DFNS/TiO₂-Cu, in which Cu NPs are located close to each other. An x-polarized total-field scattered-field (TFSF) source having a wavelength range of 200 nm to 1100 nm and E_0 of 6197.8 V m⁻¹ (for light intensity- 5.1 W cm⁻²) was used as the excitation source to mimic the photocatalysis conditions. To monitor the changes in electric field direction with wavelength, a single Cu NP over TiO₂ nanosheet was also modelled. Frequency domain field profile monitors were used to calculate the electric field distribution in all the simulations.

In-situ DRIFTS analysis

Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) measurements were performed on a JASCO FT/IR-4700 instrument with a DiffusIRTM-PIKE Technologies high-temperature reaction chamber with KBr windows. The catalyst (5 mg) was taken in a ceramic porous base crucible, which was placed inside the reactor chamber. CO₂ was filled in the reactor by flowing 20 mL min⁻¹ gas for 15 min, the light of intensity 5.1 W cm⁻² was shone and the spectra were recorded and averaged out using 2400 scans and with a resolution of 4 cm⁻¹. Then, the

gas with a composition CO_2 -10 mL min⁻¹ and H₂-10 mL min⁻¹ was filled in the reactor by flowing for 15 min and the spectra were recorded under light and dark conditions. The spectra were recorded against the baseline of the Ar filled reactor (20 mL min⁻¹) in light.



Scheme 1. Photocatalytic CO_2 reduction experimental setup, (a) sketch of pike reactor with gas lines and interaction of gas flow with the catalyst powder in the crucible; (b) focused light path diagram using the lens and mirror assembly; (c) Photocatalytic reaction setup employed for temperature measurement showing the surface of catalyst bed temperature readings (using an external thermocouple shown in magnified image) and reactor's temperature (using reactor's inbuilt thermocouple); (d) photograph of pike flow reactor (top view) showing the gas inlet, outlet and the reaction chamber with quartz window, and porous Al_2O_3 crucible containing ~5 mg catalyst.



Figure S1. High-angle annular dark field scanning transmission microscopy (HAADF- STEM) images and EDS elemental maps for the spent DFNS/TiO₂-Cu10 catalyst after 30h of reaction.



Figure S2. Size distribution of copper nanoparticle (Dp: Mean Particle Size); (a-c) DFNS/TiO₂-Cu0.05; (d-f) DFNS/TiO₂-Cu4; (g-i) DFNS/TiO₂-Cu10; (j-l) DFNS/TiO₂-Cu20.



Figure S3. HRTEM image showing two phases of Cu NPs in DFNS/TiO₂-Cu10



Figure S4. Powder X ray Diffraction (PXRD) patterns of DFNS/TiO₂, DFNS/TiO₂-Cu10 in as-prepared (ASP), reduced, spent form.



Figure S5. Pore size distribution of different catalysts using nitrogen sorption isotherms.



Figure S6. *In-situ* HERFD-XANES of oxidized DFNS/TiO₂-Cu10 catalyst during *in-situ* H₂ reduction conditions with 20 mL min⁻¹ H₂ flow at various temperatures with a ramp of 8.5 °C min⁻¹ Ti K-edge XANES spectra.



Figure S7. Comparison of activity in light and dark at same catalyst bed temperatures.



Figure S8. Variation in CO production rate at different light wavelengths (under constant light intensity, 3.1 W cm^{-2} (extinction spectra of the catalyst is shown in red)



Figure S9. Electric field enhancement and the corresponding vector diagram at different wavelengths for DFNS/TiO₂-Cu system using FDTD simulations.



Figure S10. Photoluminiscence (PL) spectra of DFNS/TiO₂, DFNS/TiO₂-Cu4 and DFNS/TiO₂-Cu10 catalysts.



Figure S11. Cu K edge X-ray absorption near edge spectra (XANES) for DFNS/TiO₂-Cu 0.05 showing the change in electronic structure of Cu on illumination at 420 and 360 nm



Figure S12. (a) Cu K-edge XANES spectra for DFNS/TiO₂-Cu0.05 and DFNS/TiO₂-Cu20 and Cu standards. Ti K-edge Gaussian curve fittings of anatase TiO_2 in the pre-peak region for (b) DFNS/TiO₂-Cu0.05 and (c) DFNS/TiO₂-Cu20 with A2/A3 ratio from the pre-edge of Ti K-edge.



Figure S13. Normalized EXAFS spectra with Fourier transformed amplitude along with the best fit theoretical plot of (a) DFNS/TiO₂Cu-0.05 (c) DFNS/TiO₂Cu-20, EXAFS spectrum oscillations of (b) DFNS/TiO₂Cu-0.05 (d) DFNS/TiO₂Cu-20 for Cu K-edge.



Figure S14. Ti K-edge X-ray absorption near edge spectra (XANES) for DFNS/TiO₂-Cu0.05 showing the change in the electronic structure of Ti on illumination at 420 and 360 nm, respectively.



Figure S15. *In-situ* DRIFTS spectra for CO_2 and $CO_2 + H_2$ conditions in light in different regions (a) higher wavenumber (b) lower wavenumber.

Entry	Sample	Ti (wt%)	Cu (wt%)
1	DFNS/TiO ₂ -Cu0.05	5.3 ± 0.5	0.03 ± 0.01
2	DFNS/TiO ₂ -Cu4	5.2 ± 0.5	3.7 ± 0.3
3	DFNS/TiO ₂ -Cu10	4.9 ± 0.5	9.1 ± 0.9
4	DFNS/TiO ₂ -Cu20	3.6 ± 0.5	18.7 ± 1.8

Table S1. Elemental composition of different catalysts by SEM-EDS

Table S2. BET surface areas and BJH pore volumes of different catalysts.

Sample	BET Surface Area (m ² /g)	BJH Pore Volume (cm ³ /g)	
DFNS/TiO ₂	446	0.60	
DFNS/TiO ₂ -Cu10 (ASP)	293	0.39	
DFNS/TiO ₂ -Cu10 (Reduced)	442	0.59	

Standard error in measurement: $\pm 10\%$ in BET Surface area, ± 0.02 in Pore Volume

S. No.	Catalyst	yst Photocatalytic Conditions Product Yield (mmol g _{act} ⁻¹ h ⁻¹		Product Selectivity (%)	Refere nce
1	DFNS/TiO ₂ -Cu10	P: 1 atm, L: Xenon lamp, 200-1100 nm, 5.1 W/cm ² , T: 269 °C, R: Flow	CO : 3601 CH ₄ :0	100	This work
2	DPC-C4-Ni	P: 1 atm, L: Xenon lamp, 400-1100 nm, 2.77 W/cm ² , T: 223 °C, R: Flow	$\begin{array}{c} {\rm CO:} 2464{\pm}40 \\ {\rm CH_4:} 140{\pm}6 \end{array}$	95 5	3
3	Ni3N	P: 1 atm, L: Xenon lamp, 2.8 W/cm ² , T: 550°C (Thermal), R: Flow	CO: 1212 CH4: NR	99 1	4
4	Ni ₁₂ P5/SiO2	P: 1 atm, L: Xenon lamp, no filter 0.8 W/cm ² , T: 280 °C, R: Flow	CO : 13.5 CH4 : NR	99.8 0.2	5
5	Nb ₂ C/Ni	P: 1 atm, L: Xenon lamp, 1.5 W/cm ² , T: 300 °C, R: Batch	CO : 250 CH4 : 1250	16.6 83.4	6
6	In2O3-x	P: 30 psi, L: Xenon lamp, 2 W/cm ² , T: 300 °C, R: Batch	CO : 238.8	100	7
7	Au/TiO ₂	P: 3.5 bar, L: Solar simulator, AM 1.5 1.44 W/cm ² , T: 150°C, R: Batch	CO : 160 CH ₄ : 10.5	93.8 6.2	8

Table S3. Comparison of the best reported photocatalytic systems employed for CO₂ reduction

8	Au/TiO ₂	P: 110 psi, L: Visible light, 0.5216 W/cm ² , T: 400°C, R: Batch	CO : 159	100	9
9	Cu ₂ O	P: 15 psi, L: Xenon lamp, 4 W/cm ² , T: 322°C, R: Batch	CO : 70.3	100	10
10	Fe@C	P: 0.7 atm, L: Xenon lamp, T: 450 °C, R: Batch	CO : 26.1	100	11
11	Ni/N-CeO ₂	P: 1 atm, L: Xenon lamp, T: 350 °C, R: Flow	CO : 20.9 CH4 : 0	100 0	12
12	FeO-CeO ₂	P: 1.77 atm, L: Xenon lamp, 2.2 W/cm ² , T: ~450 °C, R: Flow	CO : 20	97	13
13	Rh/Al Nanoantenna	P: 1 atm, L: Solar simulator, 11.3 W/cm ² , T: 200°C, R: Batch	CO : 15 CH4 : 550	3 97	14
14	Au/TiO ₂	P: 1 atm, L: Hg lamp, UV light, 0.150 W/cm ² , T: 100°C, R: Flow	CO : 4.144 CH4:0.000006	~ 100	15
15	2% Ag–0.5% Au/TNWs	P: 0.2 bar, L: Xenon lamp, 0.150 W/cm ² T: not given, R: Batch	CO : 1.813 CH ₄ : 0.035	97.7 1.86	16
16	Pd@Nb2O5	P: 1 atm, L: Xenon lamp, 2.1 W/cm ² , T: ~ 470 °C, R: Flow	CO : 1.8	100	17
17	Rh/Al ₂ O ₃	Rh/Al ₂ O ₃ P: 1 atm, L: UV LED (365 nm), 3 CO : 1.8 W/cm ² T: 350°C, Reactor – Flow CH4: 21.6		7.7 92.3	18
18	Ag-NPs/TiO2 NWs	$ \begin{array}{c} Ag-NPs/TiO_2 \\ NWs \end{array} \begin{array}{c} P: \ 1 \ atm, \ L: \ Hg \ lamp, \ visible \ light, \ 20 \\ mW/cm^2, \ T: \ 100^{\circ}C, \ R: \ Flow \end{array} \begin{array}{c} CO: \ 0.983 \\ CH_4: \ 0.00973 \\ CH_3OH: 0.013 \end{array} $		~ 98	19
19	Al@Cu2O	Al@Cu ₂ O P: 1 atm, L: Supercontinuum laser, 400-859 nm, CO: 0.36 10 W/cm ² T: 160°C, Reactor – Flow		100	20
20	Ni/SiO ₂ ·Al ₂ O ₃	$ \begin{array}{c} Ni/SiO_2 \cdot Al_2O_3 \\ T: 150^{\circ}C, R: Batch \end{array} \begin{array}{c} CO \\ CH_4 \end{array} $		2.8 97.2	21
21	In2O3-x(OH)y P: 14.1 psi, L: Xenon lamp, 160 mW/cm ² C nanorod T: 200°C, Reactor – Flow		CO: 0.2462	100	22
22	Ni-Au/SiO ₂	P: 1 atm, L: Laser (520 nm), 684 W/cm ² T: 450°C, Reactor – Flow	CO : 0.18 CH4: 0.16	53 47	23
23	Pt/NaTaO3P: 40 kPa, L: Xenon lamp, 2CO : 0.134 W/cm2, T: NR, R: BatchCO : 0.134		CO : 0.134	99	24
24	Hydrideterminated nano-silicon	P: 27 psi, L: Xenon lamp, 1.5 W/cm ² T: 150 °C, R: Batch	CO : 0.083 CH4 : 0	100 0	25
25	Cu/Pd/HyWO _{3-x} P: 1 atm, L: Xenon lamp, 2 CO : 0.041 10 W/cm ² T: 250 °C, R: Flow 10		100	26	
26	Palladiumdecorated silicon-hydride	Palladiumdecorated silicon-hydrideP: 27 psi, L: Xenon lamp, 1.5 W/cm^2 T: 170°C, R: BatchCO : 0.00001 CH4 : 00 100		0 100	27
28	RuO ₂ on silicon photonic crystal	P: 1 atm, L: Xenon lamp, 2.2 W/cm ² T: 150°C, R: Flow	CO : 0 CH4 : 4	0 100	28
29	Ni-BTO P: 4 atm, L: Xenon lamp, 0.293 W/cm ² T: 350 °C, R: Batch		CO : 0 CH4 : 103.7	0 100	29

30	Ru/Silicon Nanowire	P: 15 psi, L: Xenon lamp, 1.45 W/cm ² CO : 0 0 100 T: 93 °C, R: Flow CH4 : 0.74 0 100			30	
31	Graphene Supp. NiO/Ni	P: 1.3 atm, L: Xenon lamp, 0.2236 CO : 0 0 100 W/cm ² T: 200°C, R: Batch CH4 : 0.642 0				
32	Ni/CeO ₂	P: 1 atm, L: Xenon lamp, 0.5 W/cm ² T: 250°C, R: Flow	CO : 0 0 100 CH4 : 2.5			
33	Ti-IPA MOF	P: 1 atm, L: Xenon lamp, 0.23 CO : 0 0 1 W/cm ² , T: 200 °C, R: Batch CH ₄ : 0.033 CH_4 : 0.033		0 100	33	
34	RuO ₂ /STO	P: 1.3 bar, L: Xenon lamp, 0.108 W/cm ² T: 150°C, R: Batch	bar, L: Xenon lamp, 0.108 CO : 0 0 100 2 T: 150°C, R: Batch CH ₄ : 14.6 0 100		34	
35	Ag ₂₅ Clusters	P: 1 atm, L: Xenon lamp, 420-780, 0.183 W/cm ² , T: 100°C, R: Batch	CO : 0 CH ₄ : 0.029	0 100 35		
36	Ni/Al ₂ O ₃ ·SiO ₂	SiO2 P: 1 atm, L: LED lamp, 2.2 CO : 0 0 100 W/cm^2 T: 225°C, Reactor – CH4: 35 CH4: 35		0 100	36	
37	Rh/TiO ₂	P: 1 atm, L: UV LED (365 nm), 2.73 W/cm ² , T: 282°C, R: Flow	CO : 0 CH4: 0.028	0 100	37	

Table S4. Cu K-edge EXAFS data fitting results and parameters of DFNS/TiO₂-Cu samples

S. No.	Sample	Shell	Ν	R (Å)	D.W. factor (Å)	R-factor (%)
1	DFNS/TiO ₂ - Cu0.05	Cu-Cu	7.6±0.2	2.51±0.04	0.087±0.016	15.64
2	DFNS/TiO ₂ - Cu20	Cu-Cu	10.5 ± 0.3	2.51±0.04	0.096±0.015	14.8

$$R = \left(\sum (k^3 \chi^{data}(k) - k^3 \chi^{fit}(k))^2\right)^{\frac{1}{2}} / \left(\sum (k^3 \chi^{data}(k))^2\right)^{\frac{1}{2}}$$

Supplementary Note 1. The calculation of the quantum efficiency of the photocatalytic CO₂ hydrogenation process

Quantum Efficiency is defined as:

$$Quantum Efficiency (\%) = \frac{Produced CO molecules per unit time}{Absorbed photon numbers per unit time} \times 100$$

The no. of absorbed photons per unit time, N_{photon} is calculated from the absorption spectra of DFNS/TiO₂-Cu10 at different wavelengths (405, 447, 637 and 808nm).

$$N_{photon} = \frac{Light \, Intensity \times A\% \times Illumination \, area \times time}{Average \, single \, photon \, energy \, (E_{photon}) \times N_A}$$

In photocatalytic CO₂ hydrogenation by DFNS/TiO₂-Cu10 using different wavelengths, light intensity was $3.1 \text{W} \text{ cm}^{-2}$. A% is the absorption percentage of the catalyst at that specific wavelength. Time is 1 h (3600 sec) and N_A is the Avogadro constant.

The average single photon energy is given by:

$$E_{photon} = rac{hc}{\lambda}$$

In this equation, h is the Plank constant $6.626 \times 10^{-34} \text{ m}^2 \text{ kg s}^{-1}$, c is the speed of the light in a vacuum $(3 \times 10^8 \text{ m s}^{-1})$, and λ (meter) is the wavelength of the photon.

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