

Supporting Information

Air promotes efficient and selective CO₂ photoreduction with a molecule/semiconductor hybrid photocatalyst: the significant role of simultaneous photodegradation of organic pollutant

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1 Experimental Section

1.1 Materials and characterization

Tetracycline Hydrochloride was purchased from energy chemical. All of the reagents were used without further purification. X-ray photoelectron spectroscopy (XPS) was performed on the Thermo Scientific ESCALAB Xi+, with the Al-K α ($h\nu=1486.6$ eV) radiation to analyze the binding energy of the elements contained in the samples. All peaks were calibrated to the C 1s peak at 284.8 eV. X-ray diffraction (XRD) patterns of samples were obtained by D8 Advance with the Cu-K α radiation. Scanning electron microscope (SEM) and Energy dispersive spectrum (EDS) mapping were performed on ZEISS Sigma 300 to characterize the morphological characteristics and elemental components of the samples. Brunauer–Emmett–Teller (BET) technique were conducted on Micromeritics ASAP 2460 surface area analyzer to detect the N₂ adsorption–desorption isotherms, pore size distribution and surface area of the samples. Fourier transform infrared (FT–IR) spectra were collected on Nicolet 670 FT–IR spectroscopy to confirm the chemical compositions of the samples. UV–visible diffuse–reflection spectrometry (UV–vis–DRS) spectra were recorded on Shimadzu UV–3600i Plus to further obtain the band gap energy of the samples. Shimadzu GC2014 equipped with a TCD and FID detector was used to analyze the gas products while the liquid products were detected by ¹H–NMR spectra on Bruker Ascend 500 MHz. The UV–visible absorption spectra were collected on G9 spectrophotometer to receive the absorbance of reacted solution. Photoelectrochemical measurements were performed on the electrochemical workstation (CHI–660E), using a three–electrode system. In–situ diffuse reflectance infrared Fourier transform spectra (In–situ DRIFTS) were recorded on Bruker INVENIO–S equipped with a MCT detector. The fluorescence spectra were confirmed by Shimadzu RF–6000 fluorescence spectrometer at the excitation wavelength of 375 nm with 5.0 nm excitation and emission light bandwidths. Time–resolved emission decay spectra were recorded by Edinburgh FLS1000. The electron paramagnetic resonance (EPR) experiments were performed on Bruker EMXplus–6/1. Inductively coupled plasma–Mass Spectrometry (ICP–MS) was conducted on Agilent 7800(MS). High–Resolution Mass Spectrometry (HR–MS) was performed on Shimadzu LCMS–IT–TOF.

1.2 Synthesis of NitpyCN

The pristine carbon nitride (CN) and 4'–(4–bromophenyl)–2,2':6',2''–terpyridine were synthesized following the literatures.^{1,2} The NitpyCN was synthesized as follows. Firstly, 4'–(4–bromophenyl)–2,2':6',2''–terpyridine (100 mg) was dissolved in the dichloromethane (30 mL) solution. Then, CN (1 g) was added to the solution. After the mixture was stirred for 4h, the solvent was removed at reduced pressure. The remained solid was dried in a vacuum drying cabinet for 10 h. Then, the solid was calcined under N₂ at 300°C for 4h. After calcination, the obtained solid was washed with dichloromethane to afford a product named as tpyCN. Next, tpyCN was dried in the vacuum for 10 h. Next, acetonitrile solution (40 mL) containing tpyCN (100 mg) and methyl alcohol (10 mL) solution containing NiCl₂·6H₂O (8.38 mg) were mixed under N₂. The mixed solution was stirred at 80°C for 12h. The reaction suspension was then filtered and washed with methyl alcohol to afford NitpyCN.

1.3 Photocatalytic CO₂ reduction

Photocatalytic CO₂ reduction experiments were generally carried out in a glass tube with a volume of 45 mL. For photocatalytic CO₂ reduction experiments under high–purity CO₂ (99.999%), the catalyst (NitpyCN or CN), TEA (0.07 M) and DMA/H₂O (10 mL) solution were added to the

tube. After excluding air from the catalytic system with Ar for 15 min and subsequent high-purity CO₂ for 15 min, the tube was sealed with a rubber plug immediately. The reaction system was kept at room temperature with the white LED equipment (3STECH, $\lambda \geq 420$ nm) as the light source. The obtained gaseous products were analyzed by Shimadzu GC2014 equipped with a TCD and FID detector, while liquid products such as HCOOH were determined by ¹H NMR.

In photocatalytic CO₂ reduction in the presence of air, the hybrid photocatalyst NitpyCN, the antibiotic TC and 10 mL H₂O were added to the tube. The reaction suspension was first bubbled with Ar for 15 min. Subsequently, the reaction suspension was bubbled with mixed CO₂/air gases at a certain content of air for 15 min. Then, the tube was sealed with a rubber plug immediately. In order to achieve the adsorption-desorption equilibrium of the catalytic system, the tube was stirred in dark for 15 min before light irradiation. After that, the reaction system was kept at room temperature with the white LED equipment (3STECH, $\lambda \geq 420$ nm, 7 W) as the light source. The obtained gaseous products were analyzed by Shimadzu GC-2014 equipped with a TCD and FID detector, while the degradation efficiency of TC was determined by UV-vis absorption spectroscopy. According to Lambert-Beer law, $1-c/c_0=1-A/A_0$. Therefore, the degradation efficiency of TC is calculated by the equation of $(1-A/A_0)*100\%$. Note: c_0 and c are the concentrations of TC in the reaction solution before and after photocatalysis, respectively. A_0 and A are the initial absorbance of TC at 357 nm in the reaction solution before and after photocatalysis, respectively.

1.4 Photoelectrochemical measurements

All photoelectrochemical measurements were conducted on the electrochemical workstation (CHI-660E) with Ag/AgCl as the reference electrode, platinum as the counter electrode, and FTO glass or carbon paper loaded with samples (CN or NitpyCN) as the working electrode.

The preparation of the FTO and carbon paper working electrodes was conducted as follows. For the FTO working electrodes, a mixture consisting of 5 mg of the sample (NitpyCN or CN) and 20 μ L of Nafion was initially dissolved in 2 mL of ethanol. To ensure uniform dispersion of the samples, the mixture underwent sonication for 20 minutes, resulting in the formation of an ink. Following this, 200 μ L of the ink was precisely dispensed onto the conductive side of the FTO glass (dimensions: 6 mm \times 10 mm). The FTO glass was then allowed to dry naturally. In the case of carbon paper working electrodes, 4 mg of the sample (NitpyCN or CN) and 75 μ L of Nafion were mixed in 2 mL of ethanol. After sonication, the resulting ink was ready for application. Next, 400 μ L of the ink was applied to the conductive side of the carbon paper (dimensions: 8 mm \times 10 mm). The carbon paper was left to dry naturally in the air.

Mott-Schottky plots (M-S), Electrochemical impedance spectrum (EIS), and photocurrent responses were implemented with FTO working electrode in a three-electrode cell, using 0.5 M Na₂SO₄ as the electrolyte. In addition, the photocurrent responses were measured with the LED equipment used for photocatalytic experiments. The run time was 200 s with an interval of 20 s. The values of CB and VB were calculated as follows. According to the results of M-S, the flat band potentials (E_{fb}) of CN and NitpyCN were determined to be -1.15 and -1.20 V vs. SCE, which were equivalent to be -0.91 and -0.96 V vs. NHE ($E_{NHE}=E_{SCE} + 0.24$ V), respectively. Because CN and NitpyCN were n-type semiconductors, the value of E_{fb} was basically equal to the Fermi energy level (E_f).³ On the basis of VB-XPS results, the energy level difference (E_{vf}) between E_f and VB of CN and NitpyCN were determined to be 2.35 and 2.20 eV, respectively. Therefore, the values of VB for CN and NitpyCN were calculated to be 2.35 and 2.20 V vs. NHE, respectively. Based on the Tauc plots, the E_g of CN and NitpyCN were ascertained to be 2.75 and 2.70 V vs. NHE, respectively.

Thus, the values of CB for CN and NitpyCN were calculated to be -1.31 and -1.46 V vs. NHE.

Linear sweep voltammetry (LSV) curves and Cyclic voltammetry (CV) curves were implemented with carbon paper working electrodes in H-type electrolytic cell, using 0.5 M KHCO_3 as the electrolyte. The potentials vs Ag/AgCl are transformed to values vs RHE. $E_{\text{RHE}} = 0.197 \text{ V} + E_{\text{Ag/AgCl}} + 0.0591 \text{ V} * \text{pH}$.

1.5 In-situ DRIFTS measurements

At the commencement of the measurements, the sample underwent a 30-minute purge with N_2 to eliminate any gases adsorbed on its surface. Following this, CO_2 and water vapor were introduced into the reactor while ensuring dark conditions. Subsequently, after a duration of 30 minutes, initial spectrum was recorded in the absence of light. Ultimately, the reactor was exposed to irradiation from a 300 W Xe lamp, and spectra were systematically recorded at 5-minute intervals for 30 minutes.

1.6 EPR measurements

The samples for EPR measurements were pretreated as follows. NitpyCN (10.0 mg) was added into TC (0.5 mM) solution. After sonication for 10 min, $30 \mu\text{L}$ of the solution mixed with DMPO solution ($30.0 \mu\text{L}$). Next, the mixed solution was sucked up with a capillary tube. The capillary tube was put in a quartz tube. Finally, the quartz tube was put into the Bruker EMXplus-6/1 for trapping OH^\cdot and $\text{O}_2^{\cdot-}$. The EPR spectra were recorded in the dark and then under light irradiation for 3 min with a 300 W Xe lamp. Solvents used for OH^\cdot and $\text{O}_2^{\cdot-}$ measurements were different. For OH^\cdot trapping experiment, the solvent was H_2O . For $\text{O}_2^{\cdot-}$ trapping experiment, the solvent was CH_3OH .

2 Supplementary Fig.s and Tables

Table S1. Binding energy values of C, O, N, Cl, and Ni atoms for CN and NitpyCN.

Photocatalyst	C 1s BE (eV) (%)			N 1s BE (eV) (%)				O 1s BE (eV)	Cl 2p BE (eV) (%)		Ni 2p BE (eV) (%)				
	N-C=C	C-NH _x	C-C /C=C	π- excitation	NH _x	N-(C) ₃	C-N=C		Cl 2p _{1/2}	Cl 2p _{3/2}	Ni(II) 2p _{1/2}	Ni(II) 2p _{1/2} Satellite		Ni(II) 2p _{3/2} Satellite	
												Ni(II) 2p _{3/2}	Ni(II) 2p _{3/2} Satellite	Ni(II) 2p _{3/2}	Ni(II) 2p _{3/2} Satellite
CN	288.4 (87.0)	286.5 (3.5)	284.5 (9.6)	404.2 (1.5)	401.2 (4.6)	400.3 (16.9)	398.7 (76.9)	532.8	-	-	-	-	-	-	-
NitpyCN	288.8 (85.1)	285.7 (5.2)	284.5 (9.7)	404.1 (5.2)	401.1 (5.4)	399.9 (16.7)	398.3 (72.7)	531.8	198.8 (25.4)	197.1 (74.6)	872.9 (22.9)	879.1 (11.9)	855.5 (42.4)	860.9 (22.8)	

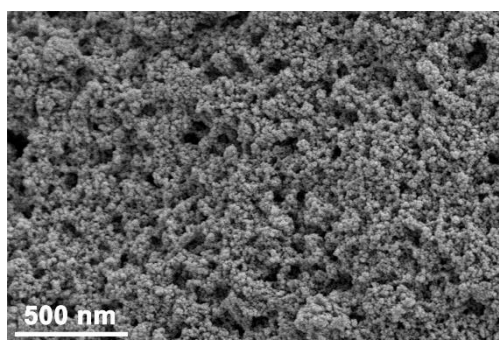


Fig. S1 SEM image of the hybrid photocatalyst NitpyCN.

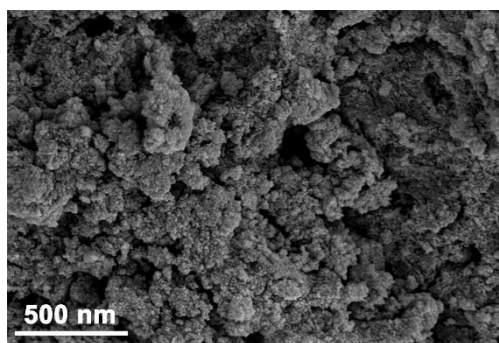


Fig. S2 SEM image of pristine CN.

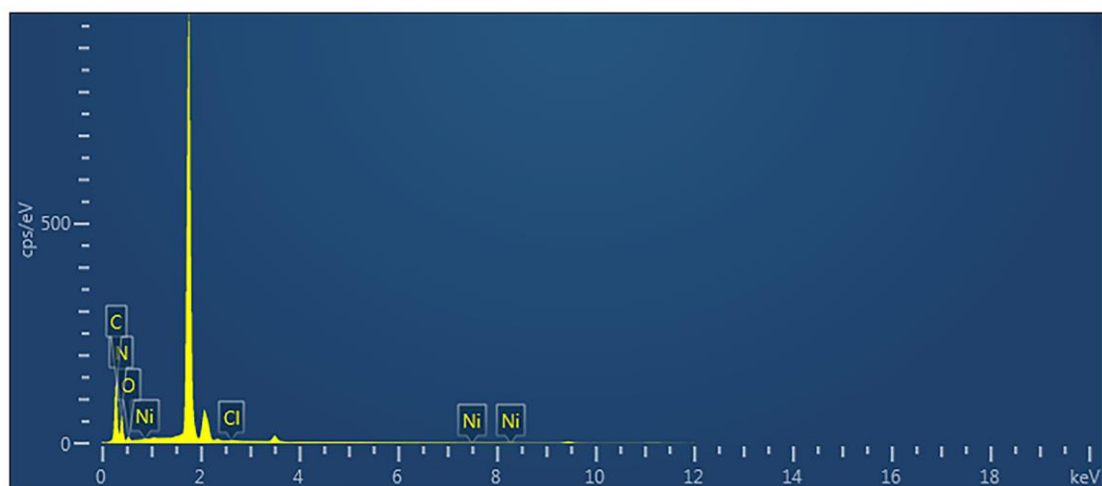


Fig. S3 The SEM-EDS plots of NitpyCN.

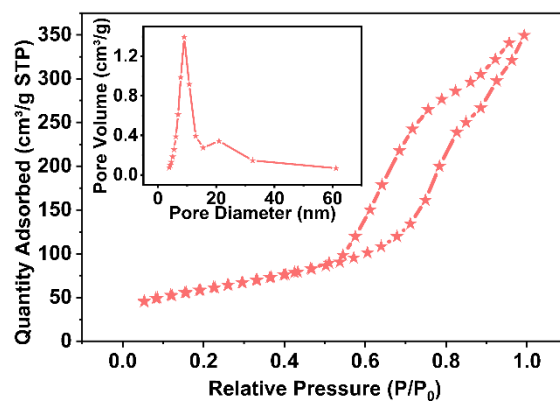


Fig. S4 N₂ adsorption–desorption isotherms of pristine CN.

Table S2. The BET surface area, pore volume, and pore size of NitpyCN and CN.

	BET Surface Area (m ² g ⁻¹)	Pore Volume (cm ³ g ⁻¹)	Pore Size (nm)
NitpyCN	203.3	0.4	8.5
CN	213.3	0.5	9.1

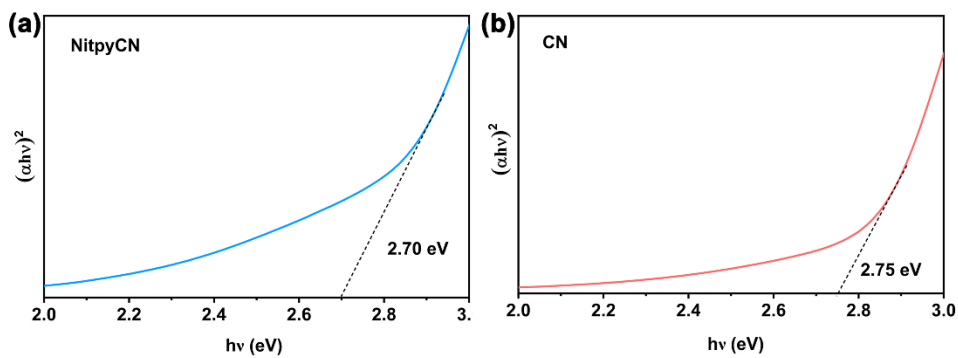


Fig. S5 Tauc plots of (a) NitpyCN and (b) CN.

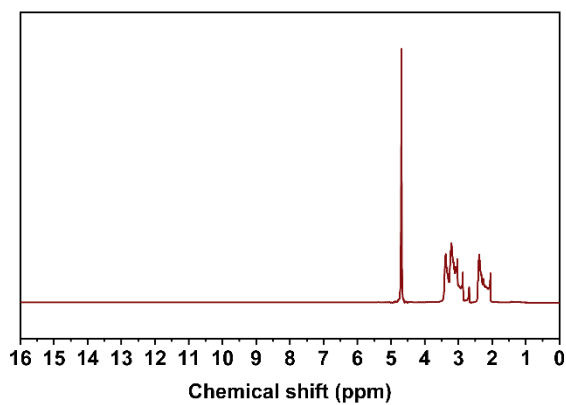


Fig. S6 ^1H NMR spectrum of photocatalytic reaction solution (400 μL) of LutpyCN by adding D_2O (100 μL) and DMSO (2.0 mg) as the internal standard.

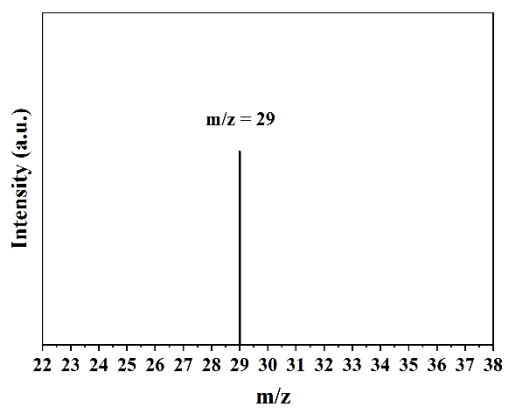


Fig. S7 The MS spectrum of isotopic labelling experiment with $^{13}\text{CO}_2$ for NitpyCN.

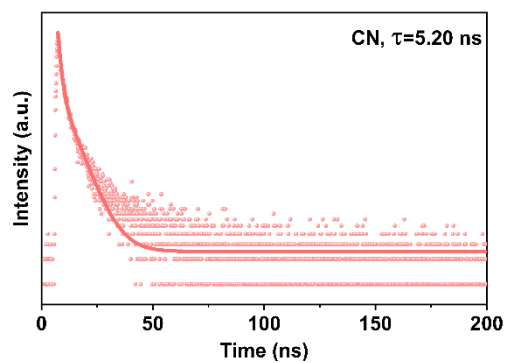


Fig. S8 Time-resolved photoluminescence spectrum of CN.

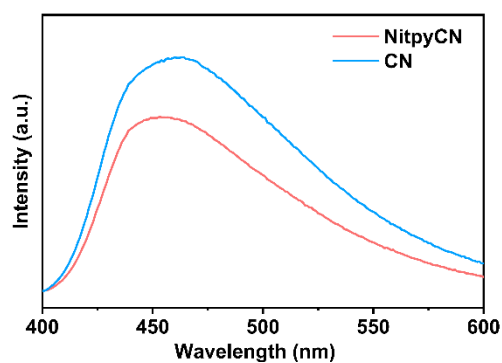


Fig. S9 PL spectra of CN and NitpyCN.

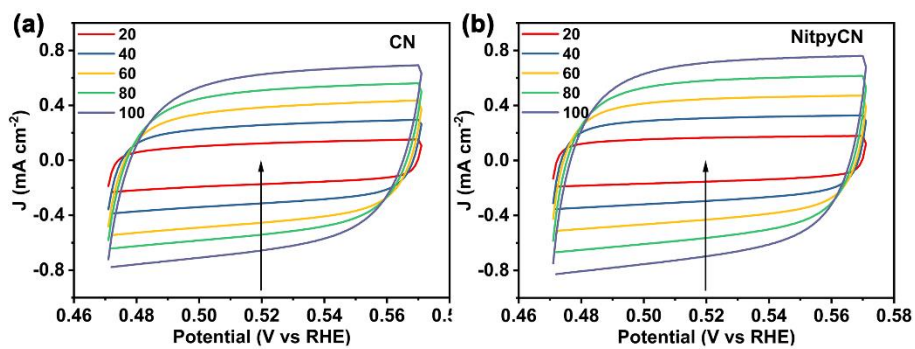


Fig. S10 CV curves at different scan rates (20, 40, 60, 80 and 100 mV s^{-1}) of (a) CN and (b) NitpyCN.

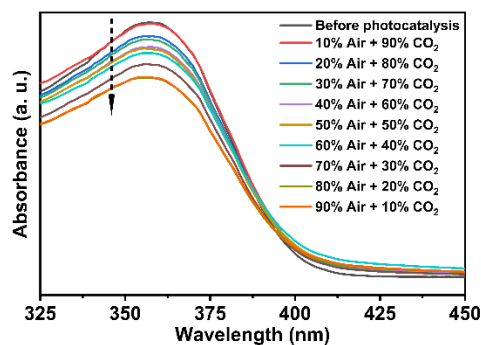


Fig. S11 The UV–visible absorption spectra of the reaction solution after photocatalysis at different volume ratios of CO_2/air .

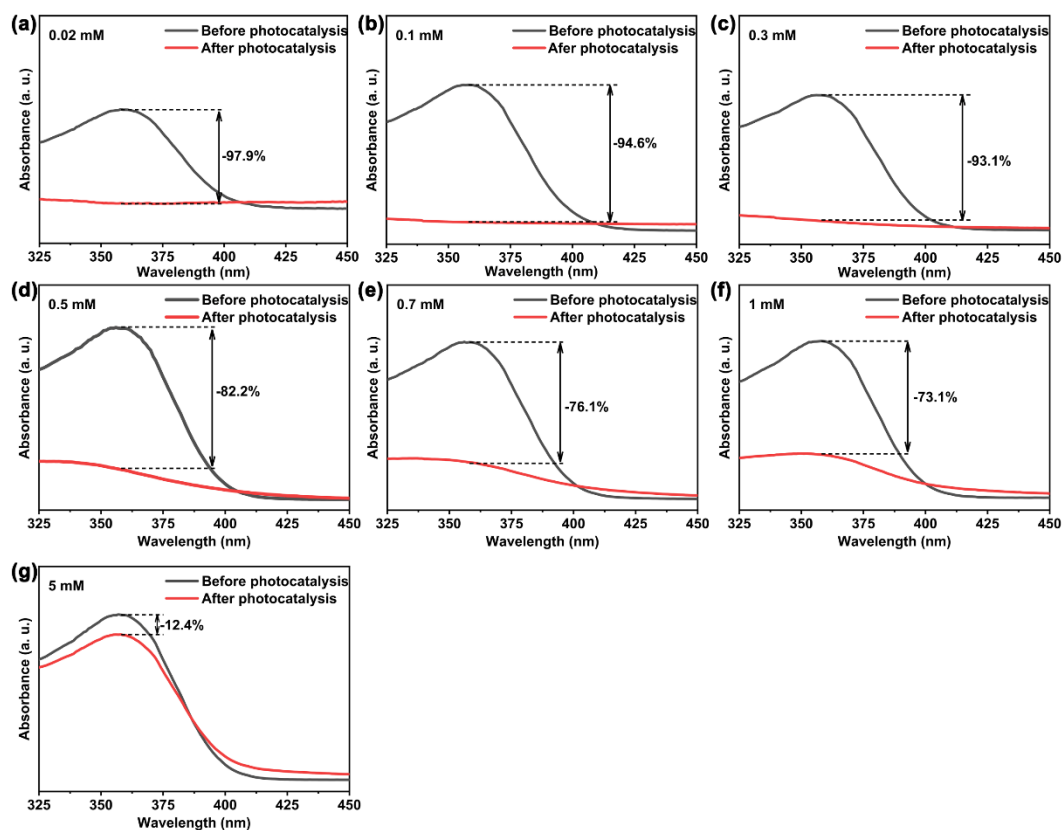


Fig. S12 The UV–visible absorption spectra of the reaction solution after photocatalysis with different concentration of TC (a) 0.02 mM (b) 0.1 mM (c) 0.3 mM (d) 0.5 mM (e) 0.7 mM (f) 1.0 mM (g) 5.0 mM.

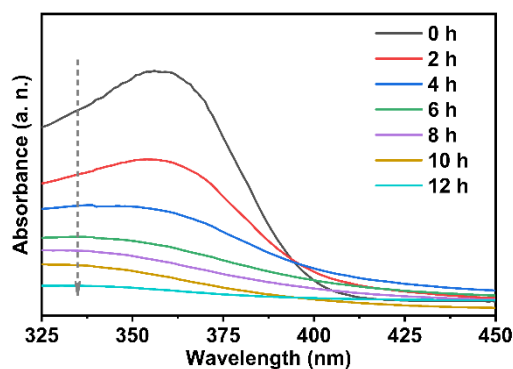


Fig. S13 UV–visible absorption spectra of the reaction solution after photocatalysis with different irradiation time.

Table S3. Comparison with recent photocatalysts for CO₂ photoreduction with simultaneous photodegradation of organic pollutants.

Entry	Catalysts	Atmosphere	Pollutants	Solvent	Products (μmol g ⁻¹)		Degradation efficiency	Reference
1	5%GQDs/ V-TiO ₂	Ar	0.025 mM Methylene blue	0.01 M NaOH aqueous solution	CH ₃ OH	105.9	99%	ACS Catal. 2016, 6, 10, 6861–6867
					C ₂ H ₅ OH	45.2		
					CH ₄	3.6		
2	1%rGO/SrTi 0.95Fe _{0.05} O _{3-δ}	Ar	0.01 mM Rhodamine B	0.02 M NaOH aqueous solution	CH ₃ OH	86.1	90%	J. Catal. 2017, 349, 218–225
					C ₂ H ₅ OH	49.1		
3	Co-BiOBr	high-purity CO ₂ gas (≥99.999%)	1.35 mM Tetracycline	Deionized water	CO	21	92%	J. Alloys Compd. 2024, 970, 172663
4	CuInZnS- Ti ₃ C ₂ T _x	high-purity CO ₂ gas (≥99.999%)	0.45 mM Tetracycline	Deionized water	CO	102	98.5%	Nano Res. 2022,15, 800-8018
This work	NitpyCN	40% CO ₂ and 60% air (Volume ratio)	0.5 mM Tetracycline Hydrochloride	Deionized water	CO	623.3	94.9%	

Table S4 Comparison with various metal complexes/carbon nitride photocatalysts for CO₂ to CO in CO₂ photoreduction. TON = n(product)/n(catalyst)

Entry	Catalysts	Other substance in the photocatalytic system	Atmosphere	TON	References
1	Coqpy@ mpg-C ₃ N ₄	0.03 M BIH, 0.03 M PhOH, and CH ₃ CN	high-purityCO ₂ gas (299.999%)	128	J. Am. Chem. Soc. 2020, 142, 13, 6188–6195
2	Fe(qpy) /C ₃ N ₄	CH ₃ CN/TEOA (4:1, v/v)	high-purityCO ₂ gas (299.999%)	155	J. Am. Chem. Soc. 2018, 140, 24, 7437–7440
3	Cotpy@ mpg-C ₃ N ₄	DMF/TEOA (v/v, 4:1)	high-purityCO ₂ gas (299.999%)	32	J. CO ₂ Util. 2022, 62, 102083
4	g-C ₃ N ₄ /[Co (dmbpy) ₃] ²⁺	ultrapure water, [Ru(bpy) ₃] ²⁺ , and CH ₃ CN/TEOA (5:1, v:v)	high-purityCO ₂ gas (299.999%)	361	ACS Catal. 2023, 13, 11376–11388
This work	NitpyCN	0.5 mM Tetracycline Hydrochloride in water	40% CO ₂ and 60% air (Volume ratio)	9.6	

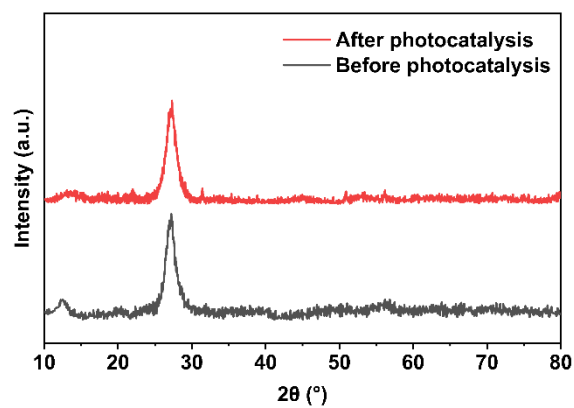


Fig. S14 XRD patterns of NitpyCN before and after photocatalysis.

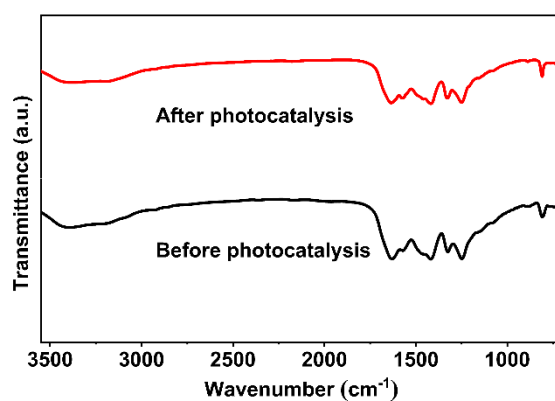


Fig. S15 FT-IR spectra of NitpyCN before and after photocatalysis.

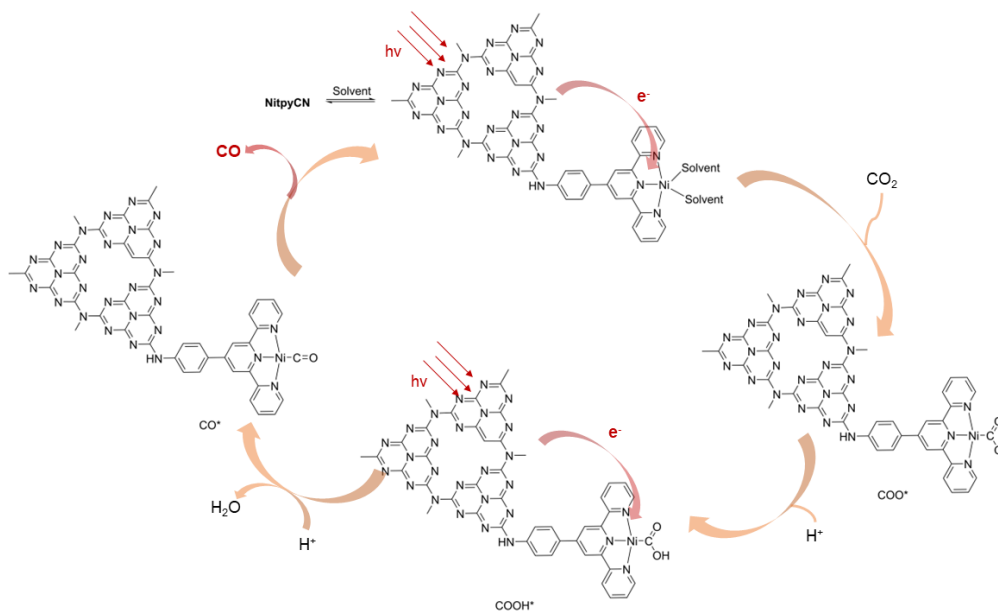


Fig. S16 Probable reaction pathway for CO₂ photoreduction using NitpyCN.

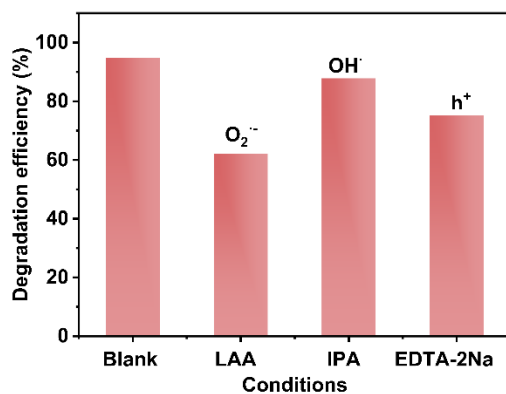


Fig. S17 The degradation efficiency of TC in the presence of various scavengers for active species. Blank: 10.0 mg NitpyCN and 0.5 mM TC under mixed CO₂/air (60% air and 40% CO₂).

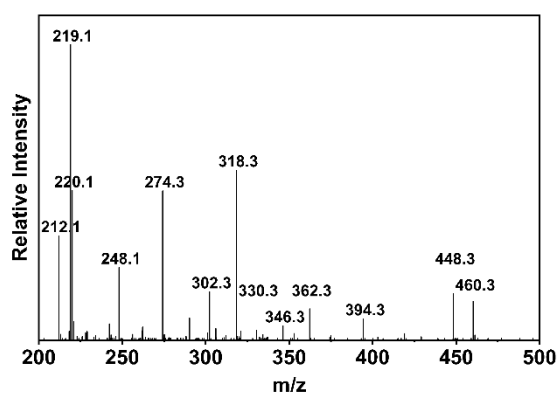


Fig. S18 HRMS of the reaction solution after photocatalysis. Conditions: TC (0.5 mM), NitpyCN (10.0 mg), light irradiation for 12 h, and water (10.0 mL) under mixed CO₂/air (60% air and 40% CO₂).

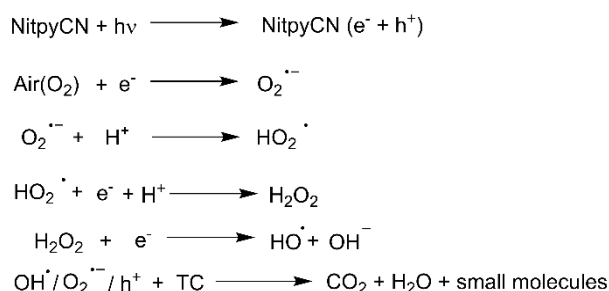


Fig. S19 Probable reactive species for photodegradation of TC.

References

1. M. Groenewolt and M. Antonietti, Synthesis of g-C₃N₄ Nanoparticles in Mesoporous Silica Host Matrices, *Advanced Materials*, 2005, **17**, 1789-1792.
2. J. Wang and G. S. Hanan, A Facile Route to Sterically Hindered and Non-Hindered 4'-Aryl-2,2':6',2''-Terpyridines, *Synlett*, 2005, **2005**, 1251-1254.
3. Y. Bai, L. Ye, L. Wang, X. Shi, P. Wang, W. Bai and P. K. Wong, g-C₃N₄/Bi₄O₅I₂ heterojunction with I₃⁻/I⁻ redox mediator for enhanced photocatalytic CO₂ conversion, *Applied Catalysis B: Environmental*, 2016, **194**, 98-104.