Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Supplemental Material: Cooperative Role of Nitrogen Defects and Cyano-group Functionalization in Carbon Nitride Towards Enhancing its CO_2 Photoreduction Activity

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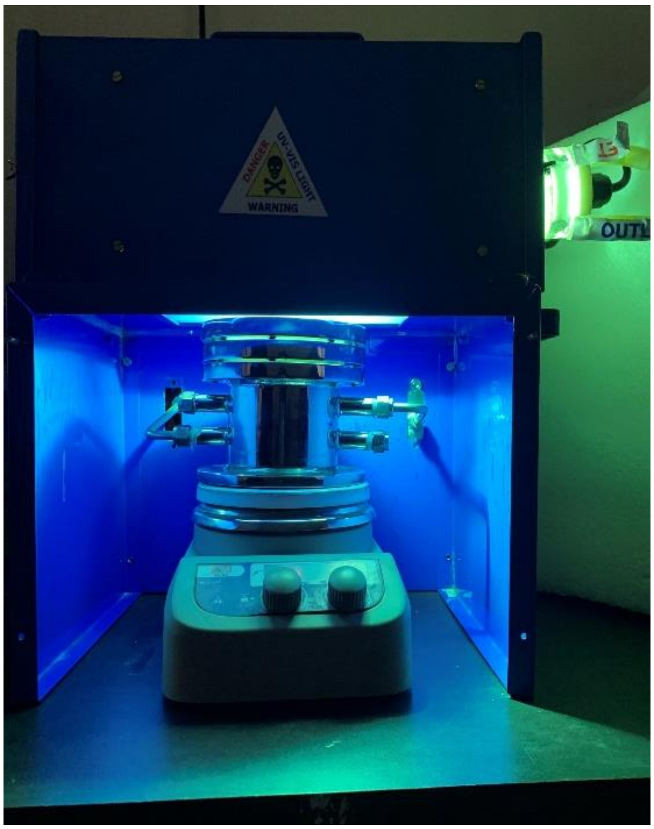

Fig. S1: Reactor Setup for Photocatalytic CO_2 reduction

Debye Scherrer equation[1] for the calculation of Crystalline size (D)

$$D = \left(\frac{k\lambda}{\beta cos\theta}\right) \qquad \text{Eq} - \text{S1}$$

where D is the size of the particle, K is known as the Scherer's constant (K=0.94), λ is the X-ray wavelength (1.54178Å), β is full width at half maximum (FWHM) of the diffraction peak, and θ is the angle of diffraction

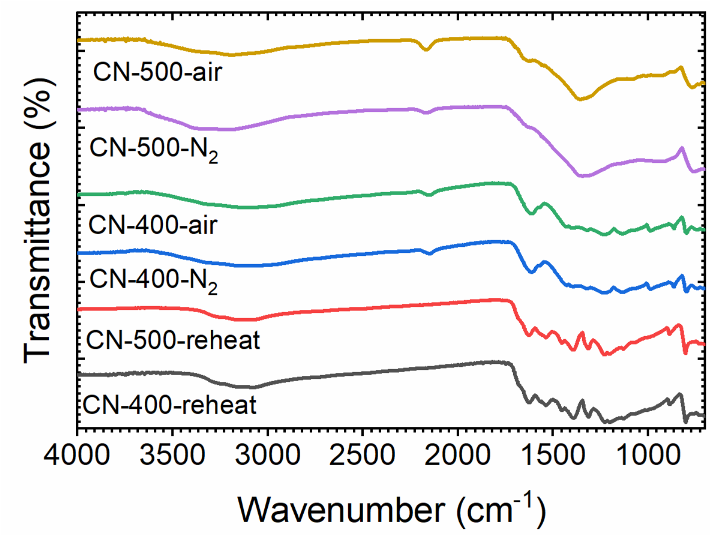

Fig. S2: FTIR Spectra for the controlled experiments for verification of generation of C≡N functionality due to the reductive role of $NaBH_4$ and temperature

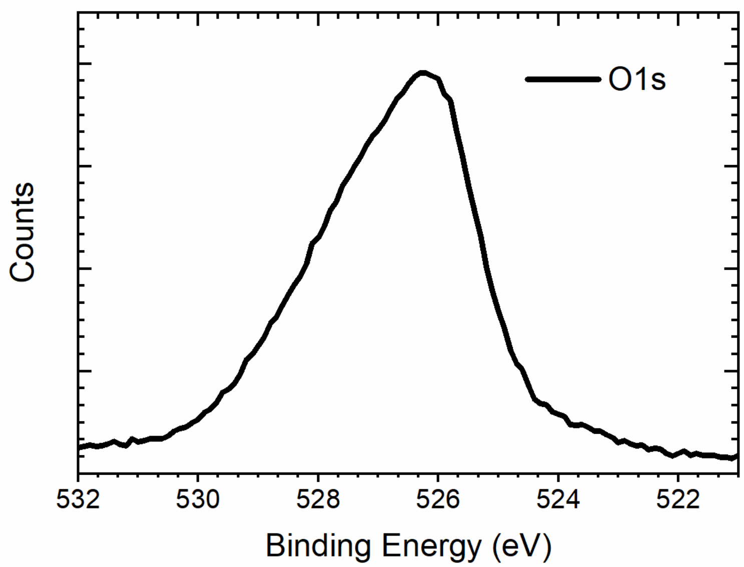

Fig. S3: High resolution O 1s spectra for CN-400-air sample

Table S1: XPS surface ratio for C/N over prepared samples.

Sample	N (type, corresponding area)		C (type, corresponding area)	
CN	397.640	16143.870	C- C	2986.049
	398.951	3443.514	N-C=N (287.9)	9945.996
	400.077	2427.067		
CN-400-air	398.681	12084.840	C- C	3634.971
	400.000	3755.500	N-C=N (288.0)	7230.412
	401.123	3270.218	C≡N (286.239)	5882.637

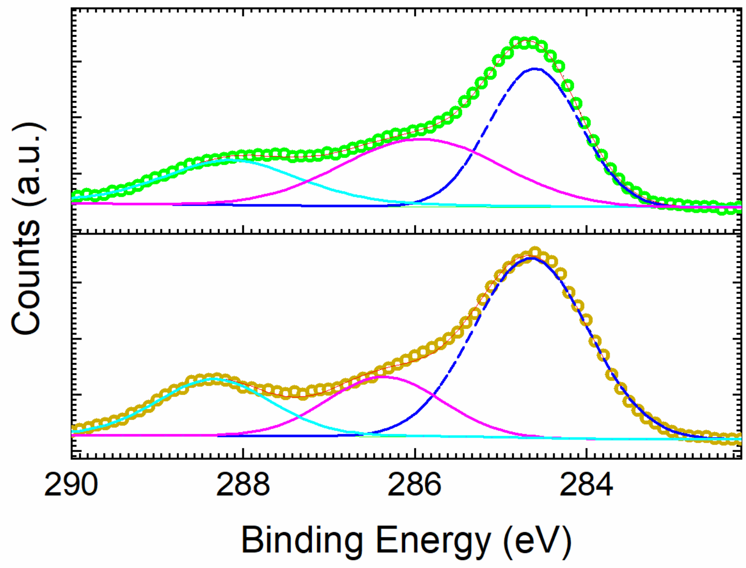

Fig. S4: High resolution C 1s spectra for CN-500-air, CN-500-N_2 sample

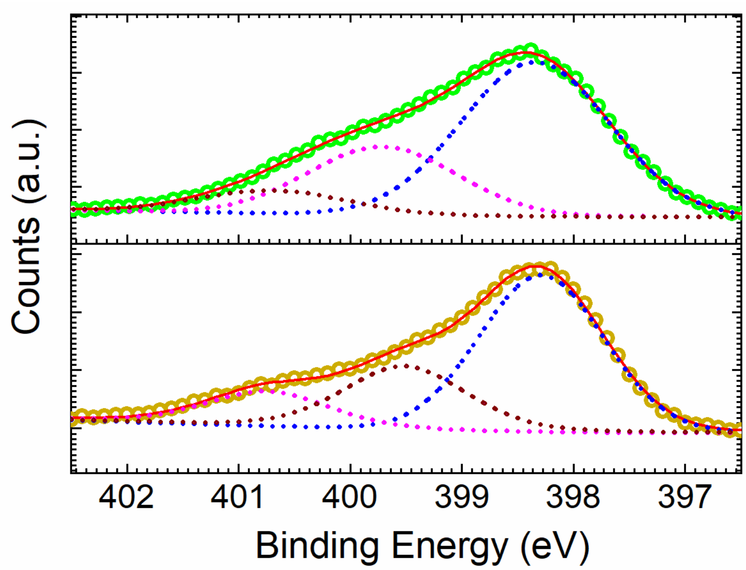

Fig. S5: High resolution N 1s spectra for CN-500-air, CN-500-N_2 sample

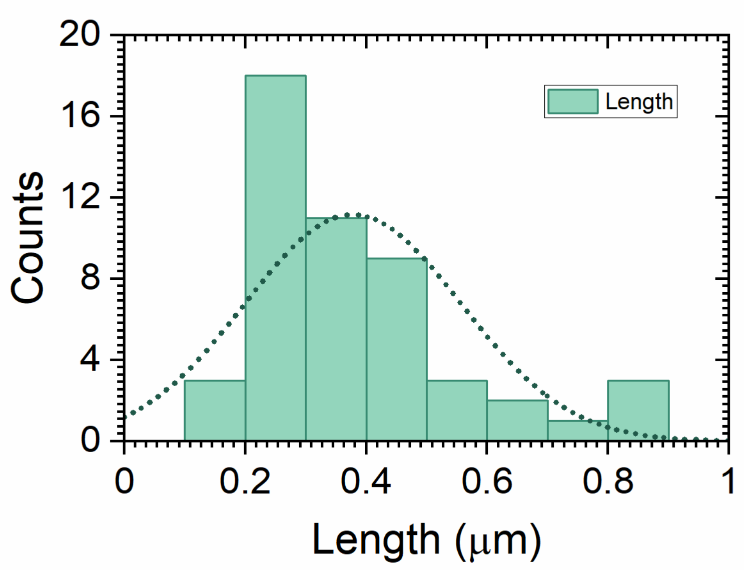

Fig. S6: Histogram for size distribution

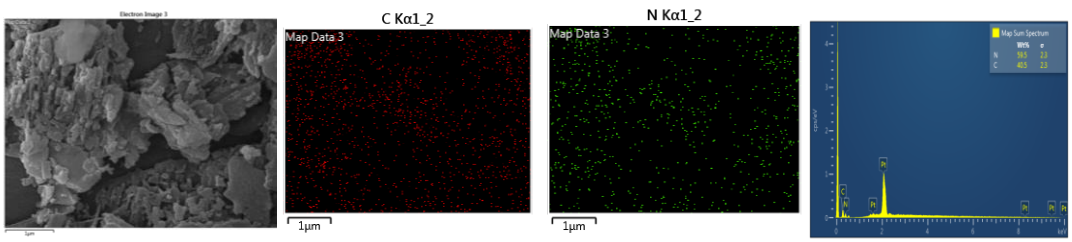

Fig. S7: Elemental mapping and distribution for CN-400-air

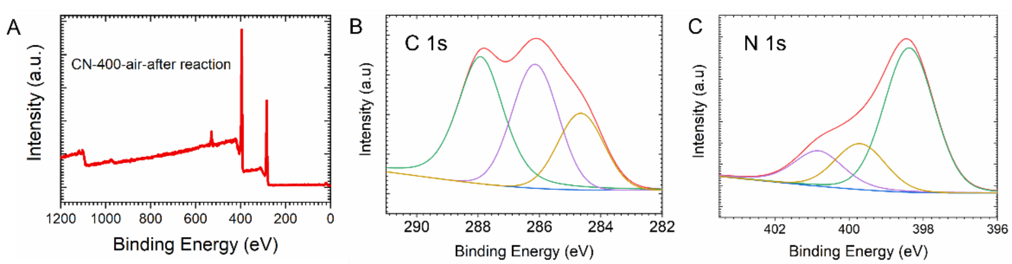

Fig. S8: XPS of carbon nitride sample after photoreduction reaction (A) full scan (B) C 1s (C) N 1s

Fig. S9: Pristine, CN-400-air, CN-500-N_2 and CN-500-air samples coated over the FTO (left to right)

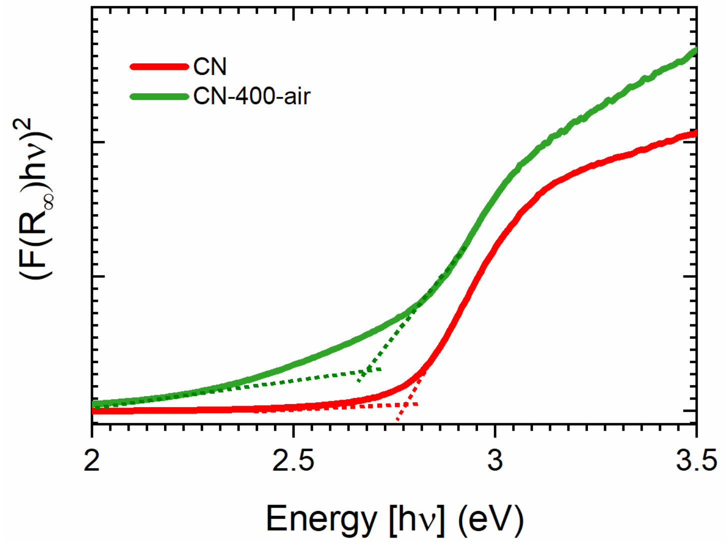

Fig. S10: Tauc plot for CN and CN-400-air samples

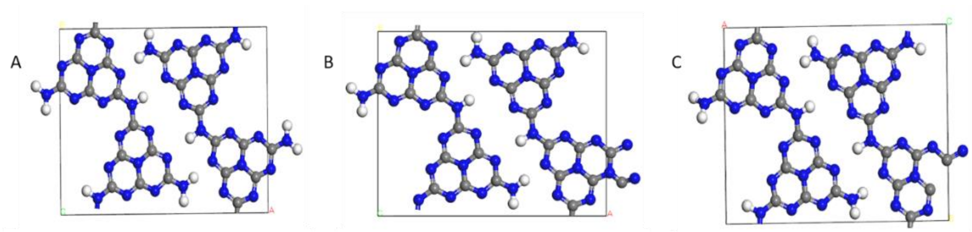

Fig. S11: DFT models for (A) Melon, (B) C≡N-Melon and (C) C≡N-N_v-Melon

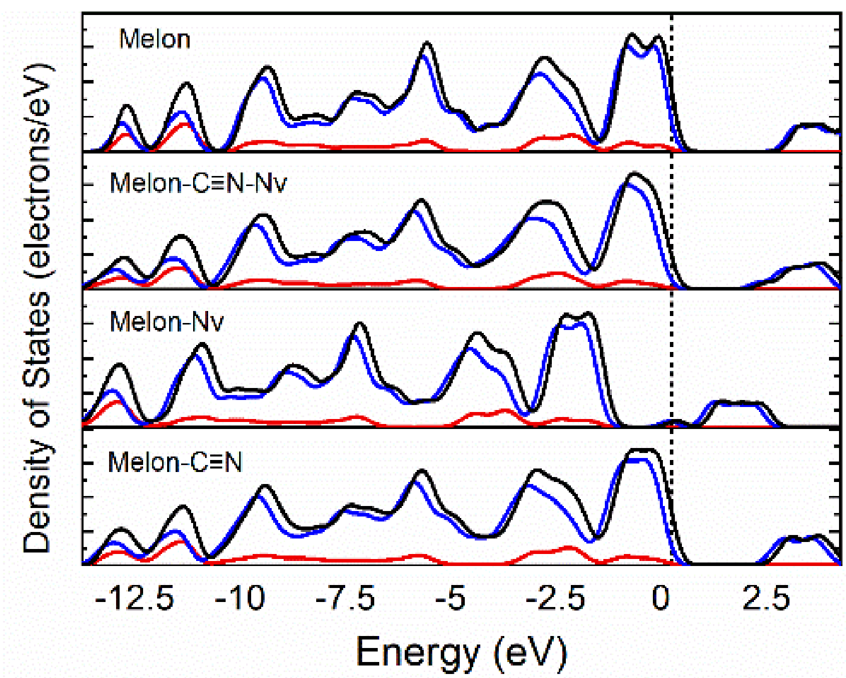

Fig. S12: Calculated PDOS for different models of carbon nitride s (red), p (blue) and total (black) contribution of energy

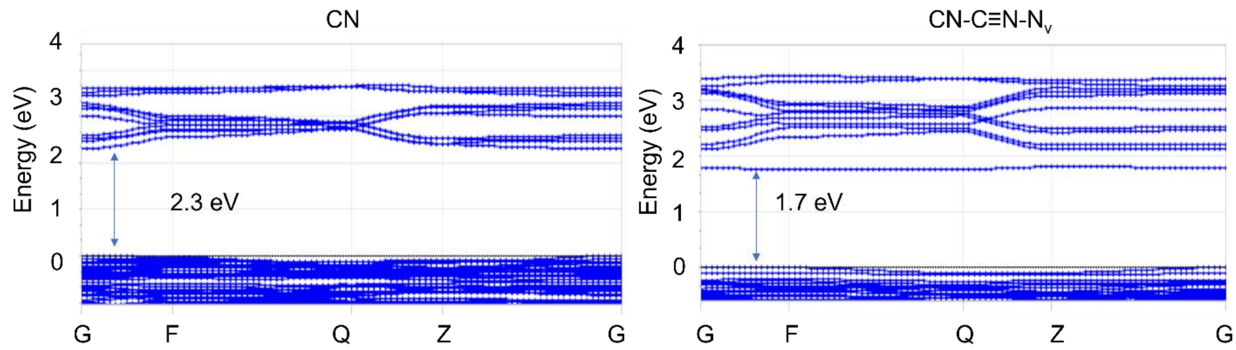

Fig. S13: Band structure profile for CN (left) and CN-C≡N-N_v (right)

Band edge positions determination:

The valance band positions were done through valance band XPS measurements (Fig. 5B main text). The VB-XPS provides the position of valance band maxima with reference to the fermi level. For the calculation of the fermi levels, Mott Schottky curves were utilized whose X-axis intercept provided the flat band potential w.r.t. Ag/AgCl. The fermi levels w.r.t. NHE were calculated using:

$$E_{fermi,\ NHE} = E_{fb,\ Ag/AgCl} + 0.22$$

With the calculated values of fermi levels, the valance band edge potentials were determined using VB-XPS given by:

$$E_{VB,\ NHE} = E_{fermi,\ NHE} + E_{VB\text{-}XPS}$$

The calculated bandgap values obtained from UV-DRS measurements were utilized to obtain the CB positions given by:

$$E_{CB,\ NHE} = E_{VB,\ NHE} + E_g$$

The calculated valance band position for CN and CN-400-air are 1.95 and 1.78 eV vs the normal hydrogen electrode (NHE), respectively and the estimated CB minima are -0.79 and -0.85 eV respectively.

Table S2: DFT calculated energy gaps and fermi levels for different models

Model	Estimated bandgap values (eV)	Fermi level position (eV)
CN	2.439	-4.881
CN-C≡N	2.109	-5.059
CN-N_v	0.377	-4.521
CN-C≡N-N_v	1.759	-4.503

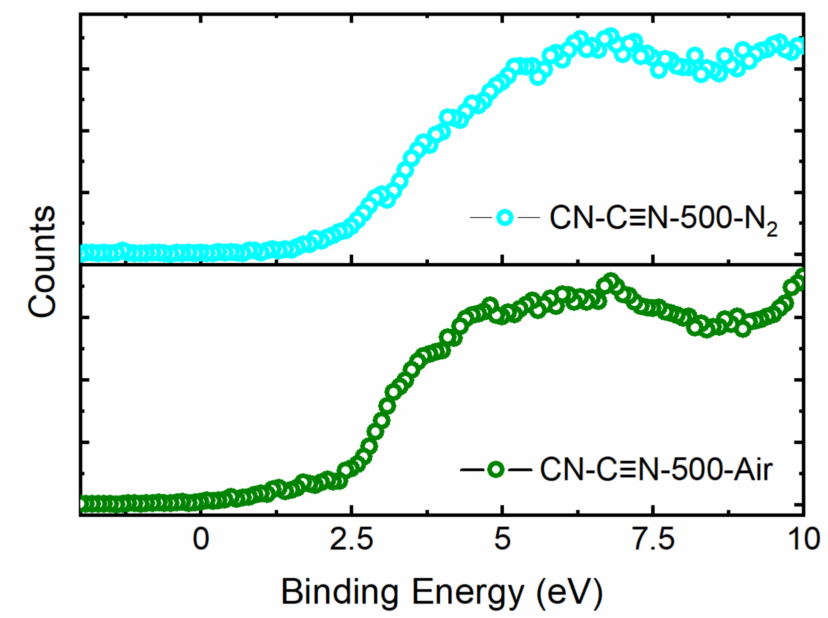

Fig S14: VB XPS for CN-500-env samples

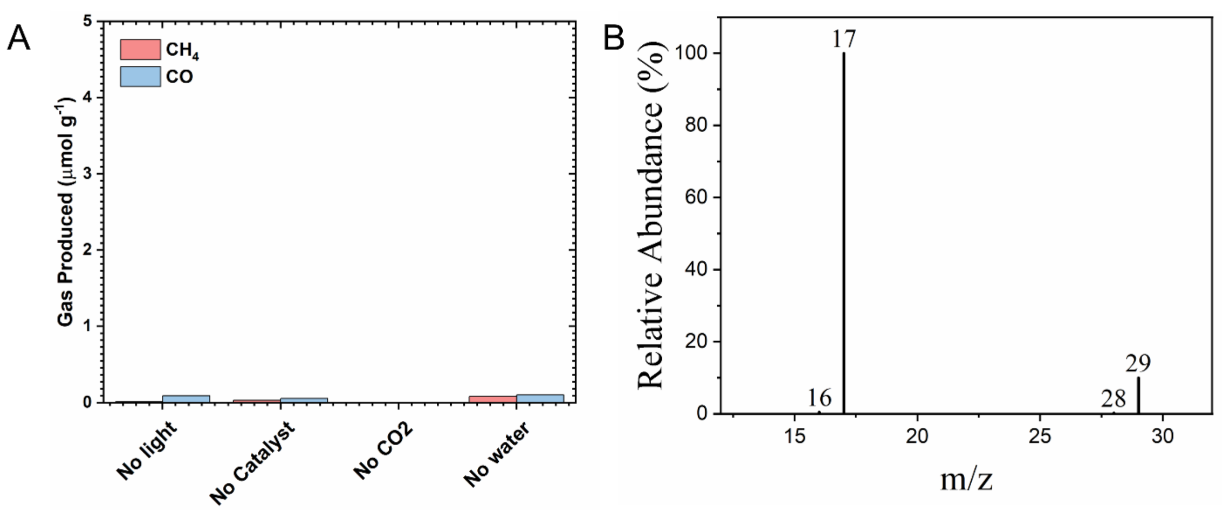

Fig S15: (A) Controlled experiments for confirmation of the CO_2 photocatalytic reduction. Photocatalytic CH_4 and CO production without light, without catalysts, without CO_2 or without H_2O on CN-400-air sample (B) Mass spectrum of photocatalytic products generated during Isotopic $^{13}CO_2$ labelled photoreduction experiment over CN-400-air

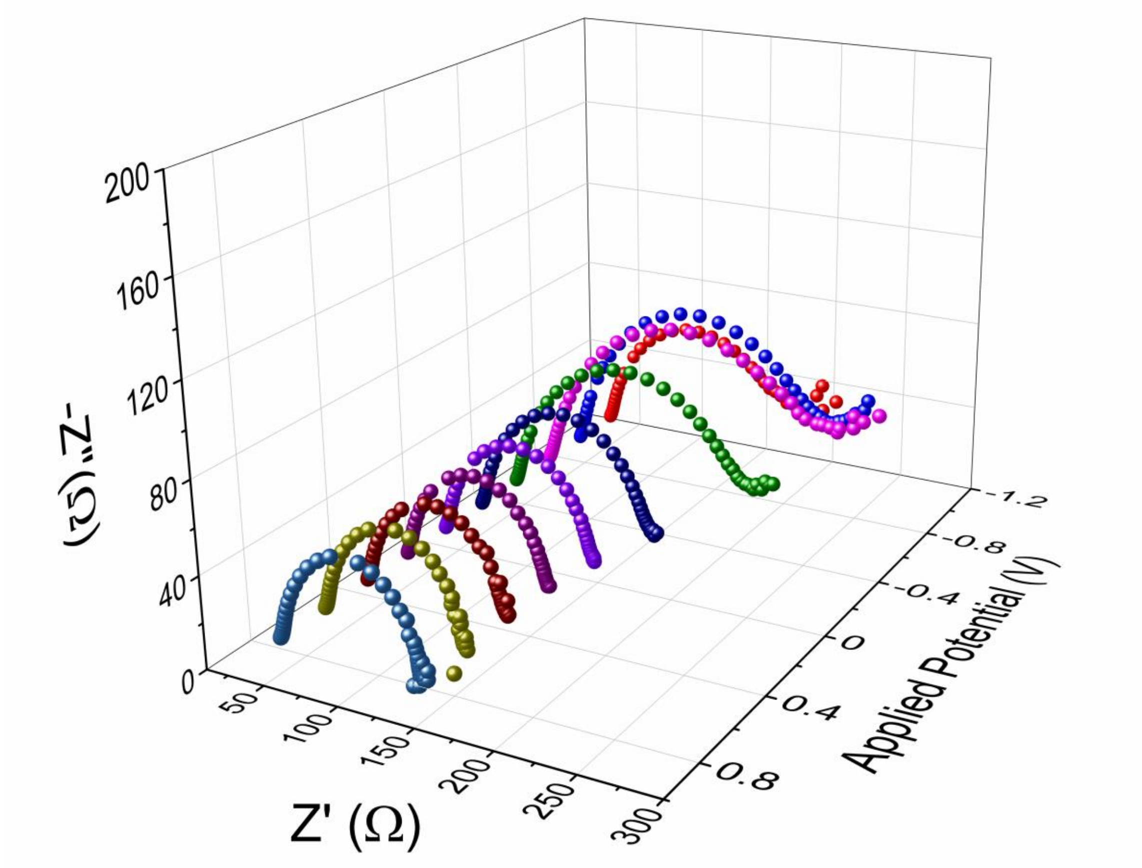

Fig S16: Electrochemical impedence spectra at different applied potentials

Table S3: Comparison of CO_2 reduction rates of CN-C≡N-N_v with reported modified carbon nitride

Catalyst Modification	Reaction condition	Product yield µmol/g-h	Reference
CN-C≡N-N_v	5 mg photocatalyst in 5mL H_2O-TEOA mixture (10%), 1.25 kg/cm^2 CO_2 pressure, room temperature, 250 W Hg lamp	CH_4 165.78 CO 0.9514	this work
Nv-rich-CN	0.03 g photocatalysts in 0.5mL H_2O,77 kPa, room temperature, 300W Xenon lamp	CO 6.61 CH_4 0.2	[2]
u-0.05PEI	catalyst 20 mg, H_2O 100 mL, 20 °C, 4 h, ultraviolet light	CO 8.215 CH_4 0.42	[3]
CCN	100 mg, 350 W Xe lamp, gas-phase CO_2 reduction	CO 1.07 CH_4 1.91	[4]
KBH-CN	0.1 g photocatalysts in 0.8 mL H_2O, 2bar, 300W Xenon lamp	CO 0.63 CH_4 1.19	[5]

CN-525	50 mg, TEOA 15 vol %, 300 W xenon lamp	CO 6.21	[6]
DCN-P	0.05 g photocatalyst in 100 mL H_2O, room temperature, 300 W Xe lamp	CO 3.94 CH_4 7.42	[7]

Table S4: Element analysis for different modified carbon nitride materials

	C (wt %)	N (wt %)	H (wt %)	N/C (atomic ratio)
CN	33.2	59.9	1.9	1.54
CN-300-N_2	33.6	59.4	2.3	1.51
CN-300-air	34.9	58.1	2.1	1.43
CN-400-N_2	34.4	58.5	2.1	1.46
CN-400-air	37.8	54.8	2.6	1.24
CN-400-reheat	33.7	59.5	2.0	1.51

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