Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

Surface defect-abundant one-dimensional graphitic carbon nitride nanorods boost photocatalytic nitrogen fixation

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1. Experimental section

1.1. Chemicals and synthesis of materials

Hydriodic acid (HI), potassium sulphate (K_2SO_4), ammonium chloride (NH_4Cl), sodium hypochlorite (NaClO), sodium hydroxide (NaOH), hydrochloric acid (HCl) sodium salicylate, sodium nitroferricyanide dihydrate, 4-(Dimethylamino)benzaldehyde, dicyandiamide, ethanol and methanol are bought from Sigma-Aldrich Australia. All chemicals are analytical reagent and used without further purification. The bulk g-C_3N_4 was prepared by the thermal decomposition of dicyandiamide. In a typical procedure, 2 g of dicyandiamide was put in a 50-mL alumina crucible and covered with a lid. Then the crucible was located in a muffle furnace and heated at 550 °C for 4 h under air atmosphere. The defective g-C_3N_4 (D-CN) was synthesized by modifying dicyandiamide with HI. Firstly, 2 g of dicyandiamide was put in a 250-mL beaker, then 25 mL of water, 25 mL of ethanol and various amount of HI (1, 1.5 and 2 mL) were added in 3 beakers. (Please note that HI may cause skin corrosion and eye irritation, thus the operation process should be extremely cared.) After that, the mixtures were strongly stirred for 4 h at 80 °C to make sure dicyandiamide and HI were mixed uniformly, and the majority of liquid were evaporated at the same time. Then the beakers were transferred into a drying oven and heated at 120 °C for 2 h to make sure only solids were remained in the beakers. The solids were then ground in an agate mortar and the rest steps were the same as the preparation of bulk g-C_3N_4. The obtained samples were named as D-CN-1, D-CN-1.5 and D-CN-2.

1.2. Characterizations

The X-ray diffraction (XRD) patterns of the samples were tested with a Bruker D8 Discover XRD with intense Cu *Kα* radiation (40kV and 40mA, λ=1.5406 Å) at room temperature. The morphology observation on the materials were carried out using a Zeiss Supra 55VP scanning electron microscope (SEM), with an operating voltage of 5 kV. TEM image of D-CN-1.5 was obtained from a FEI T20 Tecnai TEM. The X-ray photoelectron spectroscopy (XPS) (Thermo Fisher Scientific K-Alpha+) and X-ray fluorescence (XRF) spectrometer (PANalytical energy-dispersive X-ray fluorescence) were used to examine the composition of obtained materials. The UV-vis diffuse reflectance spectra (DRS) of prepared samples was obtained from a Perkin Elmber Lambda 950 UV/VIS/NIR spectrometer, using high-purity barium sulfate ($BaSO_4$) as the blank reference. A Fourier Transform Infrared (FT-IR) Spectroscopy (Nicolet 6700 FTIR) was used to characterize the functional moieties of prepared samples. Photoluminescence (PL) spectra were obtained from a Shimadzu RF-6000 fluorescence spectrometer excited at 325 nm. For time-resolved PL measurement a 405-nm wavelength, 20-MHz pulsed laser was used as excitation source. The lifetimes were collected using single photon counting module (Excelitas SPCM-AQRH) and a time correlation counting module (Picoharp 300). Data was fitted with exponential function to drive the lifetime values. The photocurrent, electrochemical impedance spectroscopy (EIS) and Mott-Schottky curves of the samples were obtained from an electrochemical working station (CHI-760E) in 0.1 M Na_2SO_4

solution. The counter electrode was a Pt wire, and the reference electrode was an Ag/AgCl electrode. The working electrodes were prepared as follow: 7 mg of samples and 0.7 mL ethanol were mixed in 5 mL cuvettes; after that the cuvettes were sonicated for 4 h to disperse the samples in the solvent homogeneously; then the suspension was evenly coated on indium-tin oxide (ITO) glasses (5 × 2 cm) and dried in air for 12 h. When testing photocurrent, the light was provided by a 300 W Xenon lamp (HSX-F300, Beijing NBET Technology Co., Ltd) and its intensity was 600 mW/cm^2, and no voltage was used. EIS was tested in the frequency from 0.01 to 1×10^5 Hz the initial voltage was 0.5 V and the amplitude was 0.005 V. The Mott-Schottky curves were obtained from the technology of impedance-potential, during which the voltage was from -1.5 to 1.5 V, and the frequency was 1000 Hz. A Bruker EMX X-Band ESR spectrometer was used to test the electron spin resonance (ESR) spectra of samples.

1.3. Photocatalytic nitrogen fixation performance

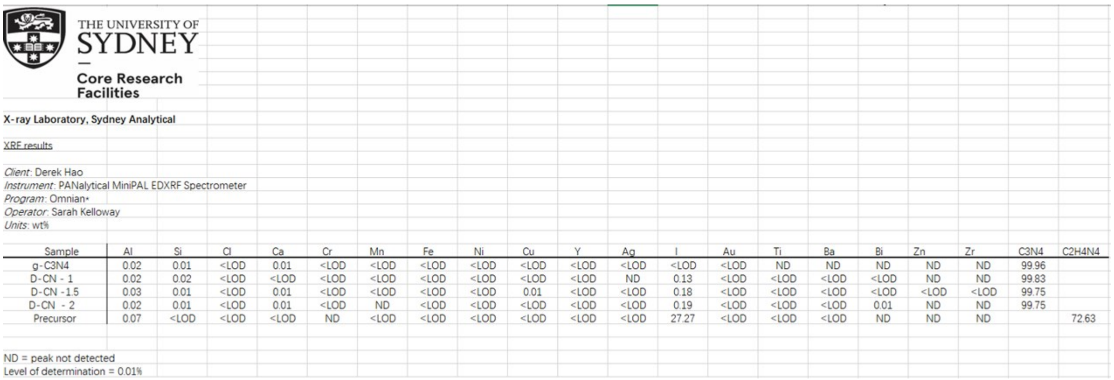
The photocatalytic nitrogen fixation performance was carried out with a self-made quartz reactor under simulated sunlight irradiation. During the reaction process, the light intensity was 600 mW/cm^2 and it was measured by a radiometer. Firstly, 200 mg of samples was weighted and put into the reactor. Then 95 mL of 0.1 M K_2SO_4 solution and 5 mL of methanol was added. The reactor was then closed and N_2 was bubbled in to remove air for 2 h with magnetic stirring. After that, the gas-out tube was closed and N_2 was kept bubbling in and the light was on. The photocatalytic reaction lasted 8 h and 2 mL of liquid was sampled every 2 h. The concentration of ammonium was measured by UV-VIS spectrometer by indophenol blue method at 667 nm. Firstly, the liquid was centrifugated and 1 mL of solution was sampled. Then 0.25 mL of NaOH solution (which contains 0.05 g/L NaOH and 0.1 mL/L NaClO) and 0.25 mL of sodium salicylate (which contains 1 g/L sodium salicylate, 2 mg/L sodium nitroferricyanide dihydrate and 25 mg/L NaOH) was added. The absorbance of the solution was measured in 2 h. The calibration curve was obtained by measuring various NH_4Cl solution ($y = 1.80737x - 0.08037$, $R^2 = 0.9998$). The UV-VIS spectrometer method was also used to detect hydrazine, where the color reagent consisted with 0.5 g of 4-(Dimethylamino)benzaldehyde, 2.5 mL of HCl and 25 mL of ethanol. 2 mL color reagent and 2 mL of sample solution were mixed and the absorbance at 458 nm was recorded. The calibration curve was obtained by measuring various N_2H_4 solution ($y = 1.206x + 0.0174$, $R^2 = 0.9995$).

1.4. DFT calculation

In this study, all the computations about those structures and energies were based on the standard DFT by using Vienna ab initio Simulation Package (5.4.4 VASP).[1] The electron exchange correlation functional was treated through the generalized gradient approximation (GGA) with the revised Perdew-Burke-Ernzerhof (RPBE).[2] The 450 eV energy cutoff was adopted and Brillouin zone was sampled with a 3×3×1 k-points using the Monkhorst-Pack scheme grid for geometry optimization and self-consistent calculations. A vacuum space exceeds 15 Å was employed to avoid the interaction between two periodic units. The atomic position was fully relaxed until the maximum force on each atom was less than -0.02 eV/A and 10^{-5} eV. And thermal and zero-point energy (ZPE) corrections were calculated over Γ points.[3] The van der Waals interaction has been considered using the DFT-D_3 scheme.[4]

Element Sample	$g\text{-}C_3N_4$	D-CN-1.5
C	40.54	41.87
N	56.72	55.32
O	2.74	2.81

Table. S1 The atomic concentration tabel of g-C3N4 and D-CN-1.5



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Core Research Facilities

X-ray Laboratory, Sydney Analytical

XRF results

Client: Derek Hao
Instrument: PANalytical MiniPAL EDXRF Spectrometer
Program: Omnian+
Operator: Sarah Kelloway
Units: wt%

Sample	Al	Si	Cl	Ca	Cr	Mn	Fe	Ni	Cu	Y	Ag	I	Au	Ti	Ba	Bi	Zn	Zr	C3N4	C2H4N4
g-C3N4	0.02	0.01	<LOD	0.01	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	ND	ND	ND	ND	ND	99.96	
D-CN - 1	0.02	0.02	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	ND	0.13	<LOD	<LOD	<LOD	<LOD	ND	ND	99.83	
D-CN -1.5	0.03	0.01	<LOD	0.01	<LOD	<LOD	<LOD	<LOD	0.01	<LOD	<LOD	0.18	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	99.75	
D-CN - 2	0.02	0.01	<LOD	0.01	<LOD	ND	<LOD	<LOD	<LOD	<LOD	<LOD	0.19	<LOD	<LOD	<LOD	0.01	ND	ND	99.75	
Precursor	0.07	<LOD	<LOD	<LOD	ND	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	27.27	<LOD	<LOD	<LOD	ND	ND	ND		72.63

ND = peak not detected
Level of determination = 0.01%

Table. S2 The XRF results of g-C3N4 and D-CN samples.

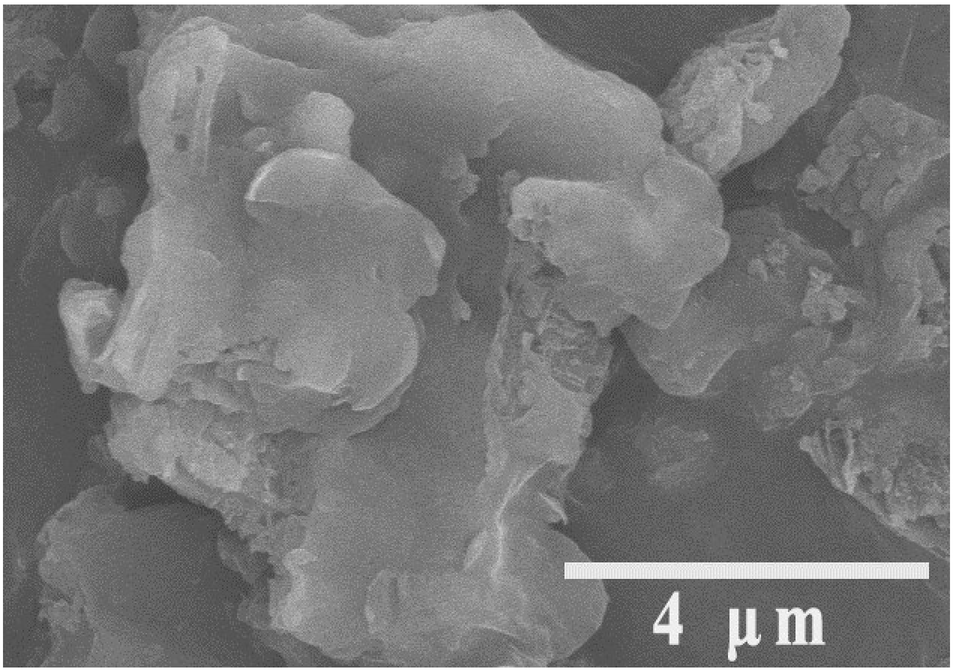

Figure S1. SEM image of bulk $g\text{-}C_3N_4$.

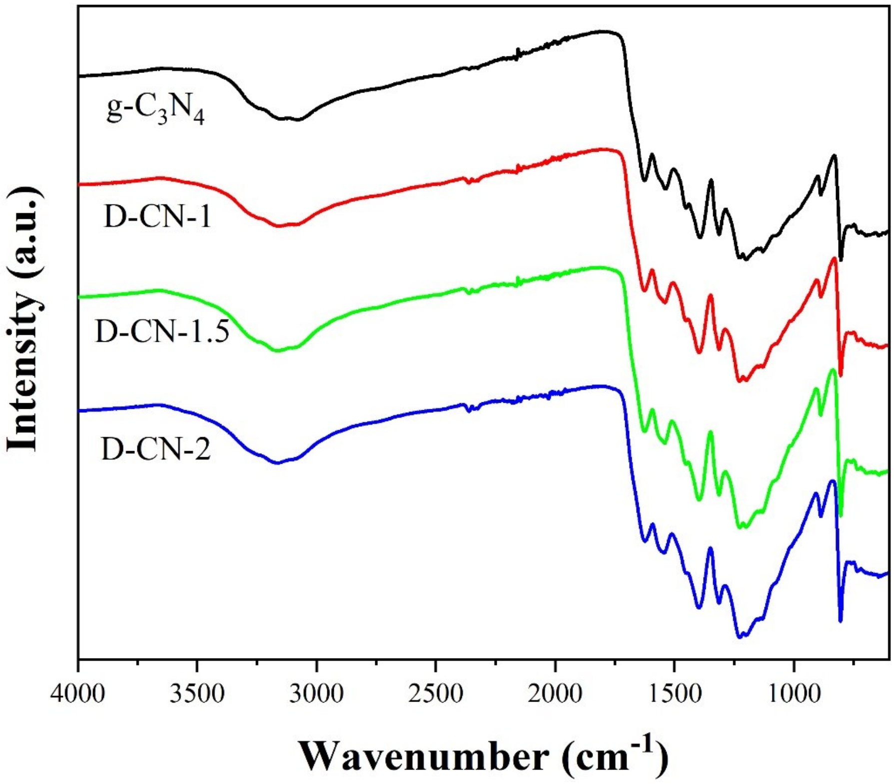

Figure S2. Comparison of FTIR spectra.

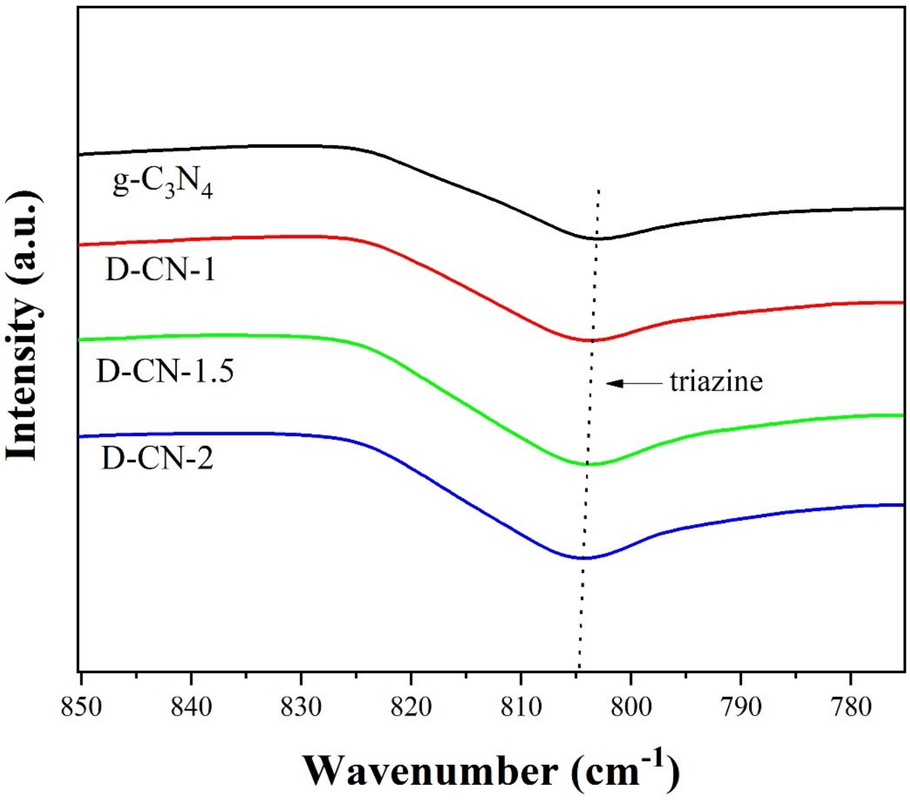

Figure S3. Comparison of FTIR spectra.

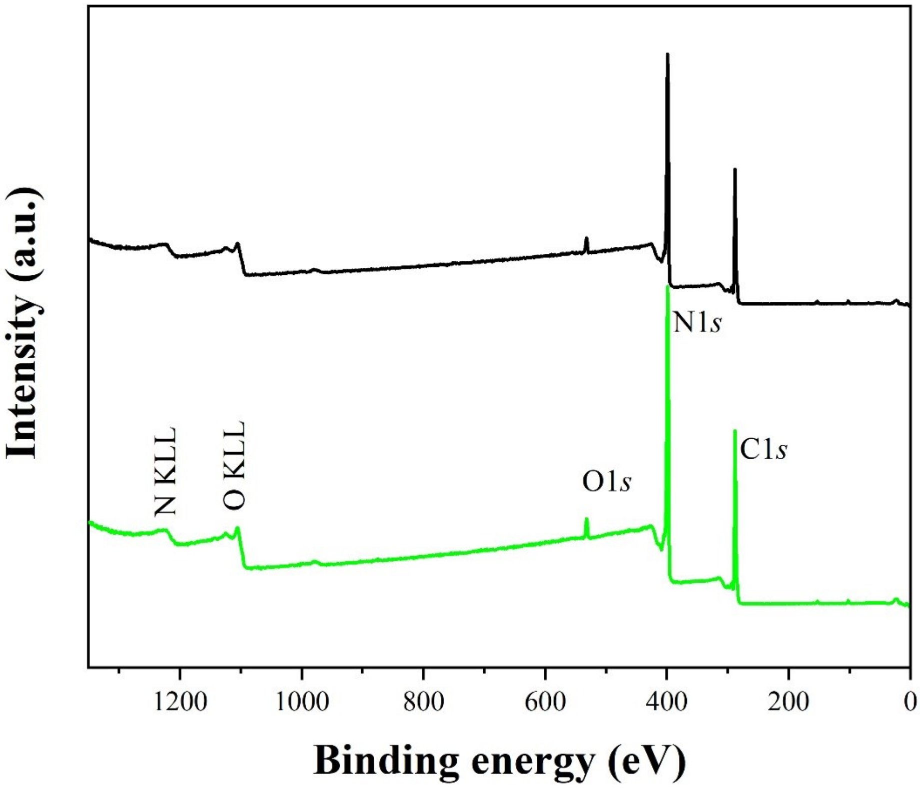

Figure S4. XPS survey spectra of g-C_3N_4 and D-CN-1.5.

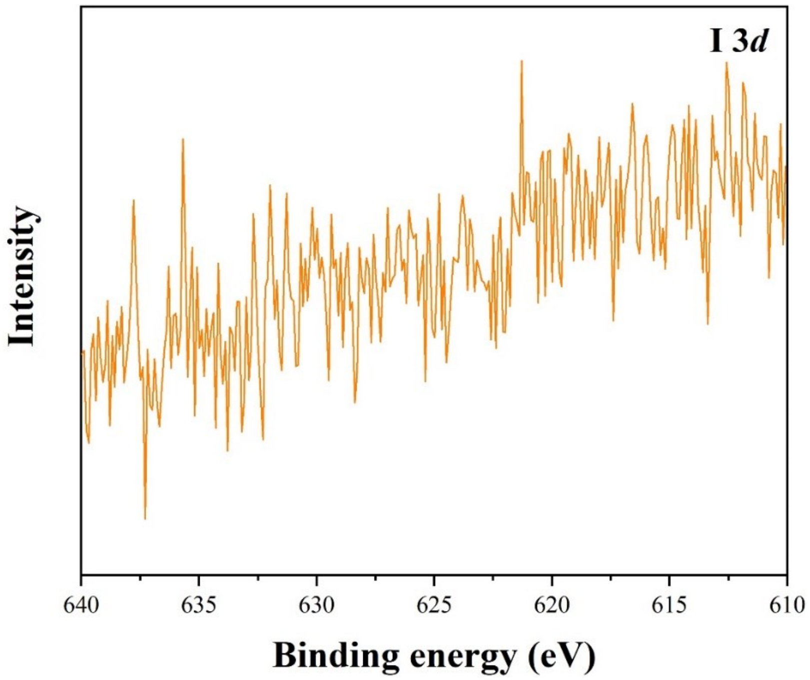

Figure S5. XPS spectra of iodine in D-CN-1.5.

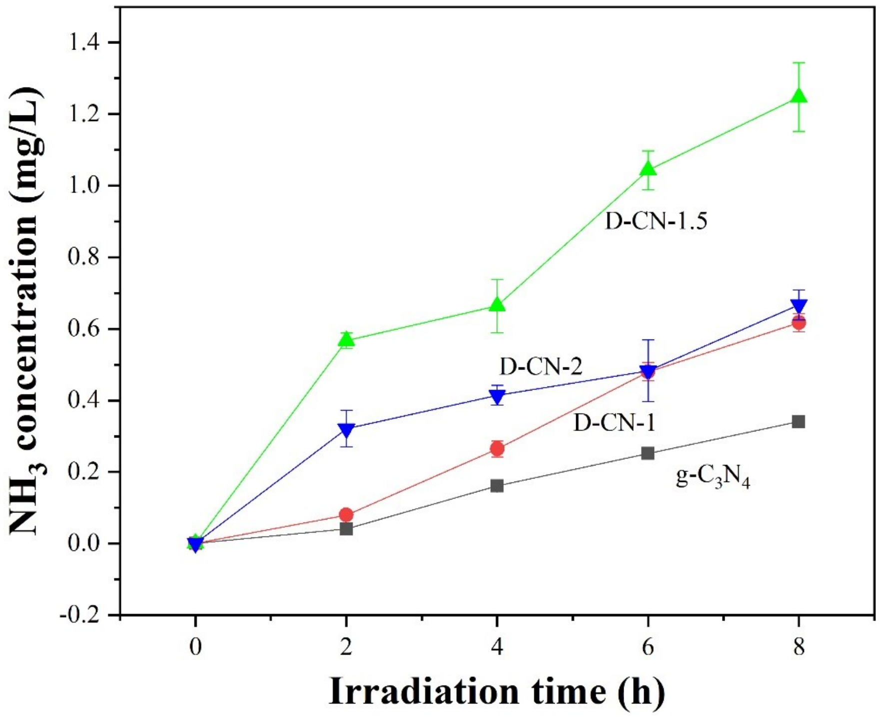

Figure S6. Time dependent NH_3 yield curve

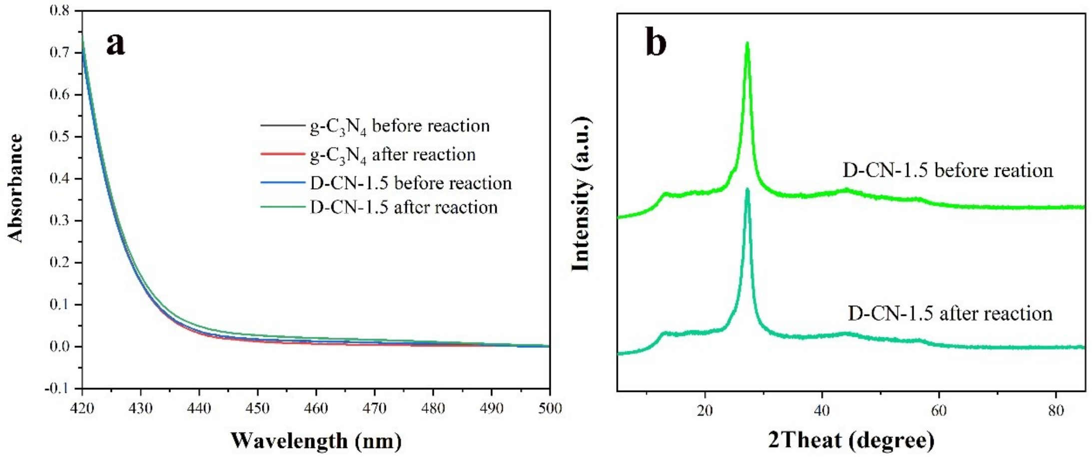

Figure S7. (a) UV-vis spectra of the N_2H_4 detection results, and the XRD patterns of D-CN-1.5 before and after reaction.

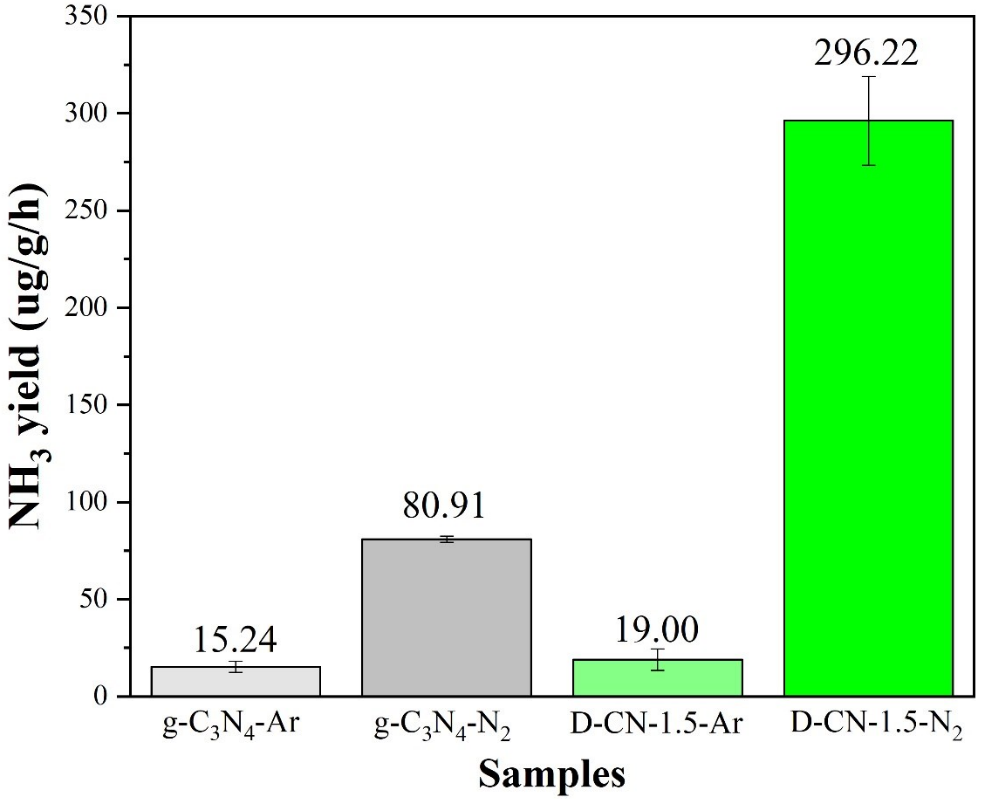

Figure S8. The NH_3 yield comparation of N_2 and Ar bubbled into the reaction system.

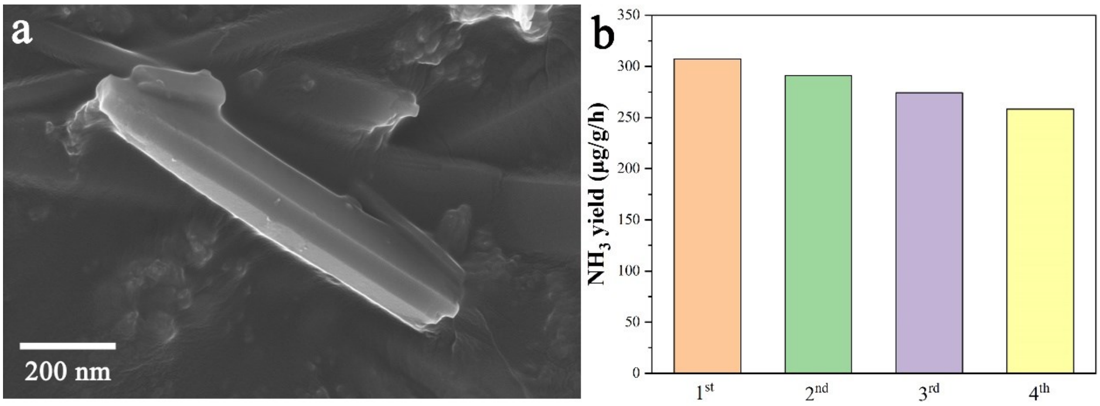

Figure S9. (a) The SEM image of D-CN-1.5 after adsorption. (b) Cycle stability of D-CN-1.5 in four cycle.

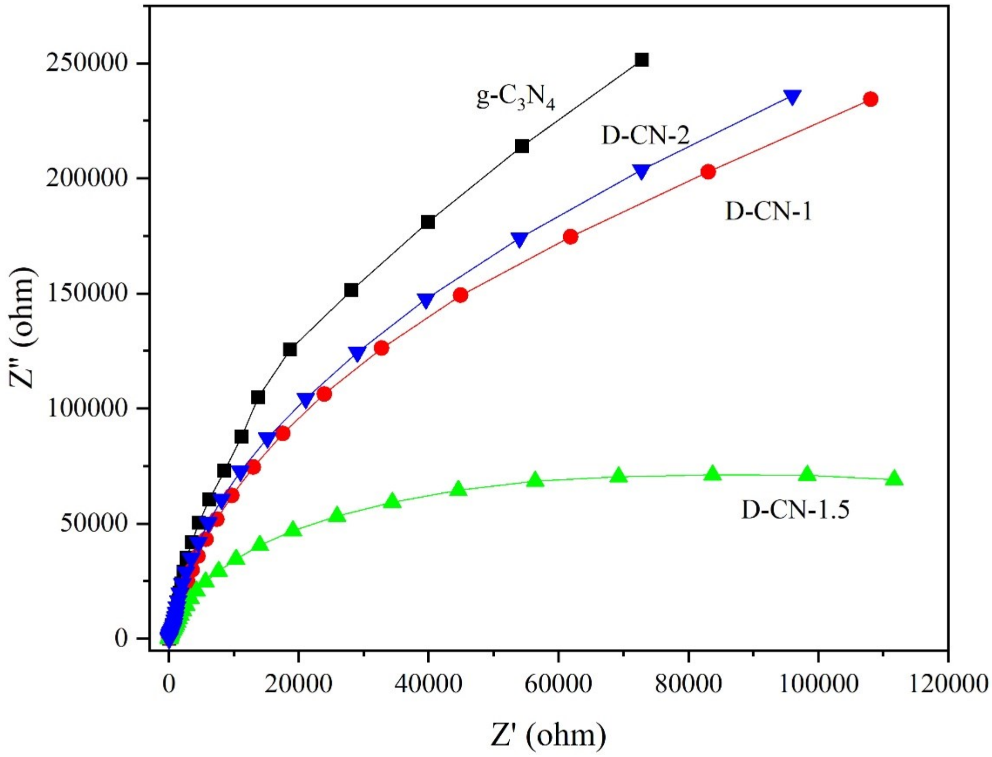

Figure S10. ESI of prepared samples.

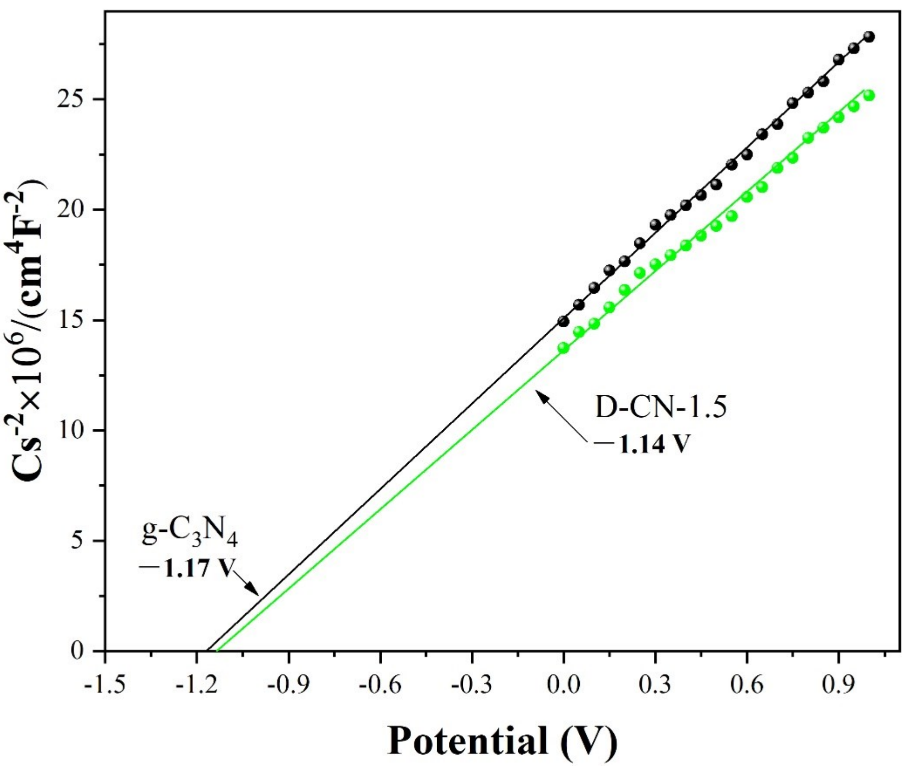

Figure S11. Mott-Schottky plots of g-C_3N_4 and D-CN-1.5 obtained at the frequency of 1 kHz.

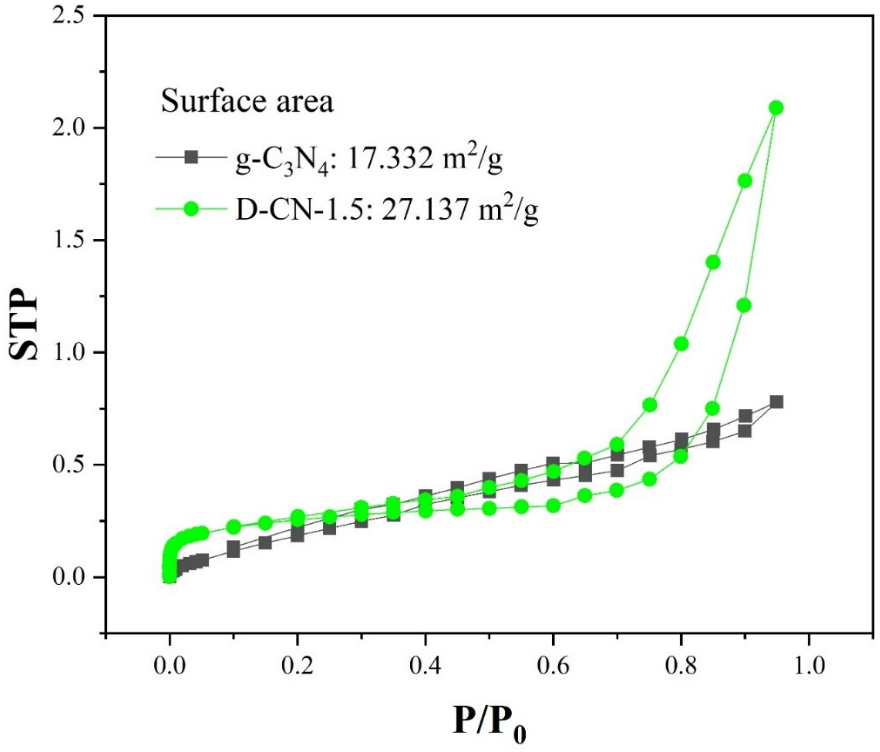

Figure S12. N_2 adsorption-desorption isotherm of g-C_3N_4 and D-CN-1.5

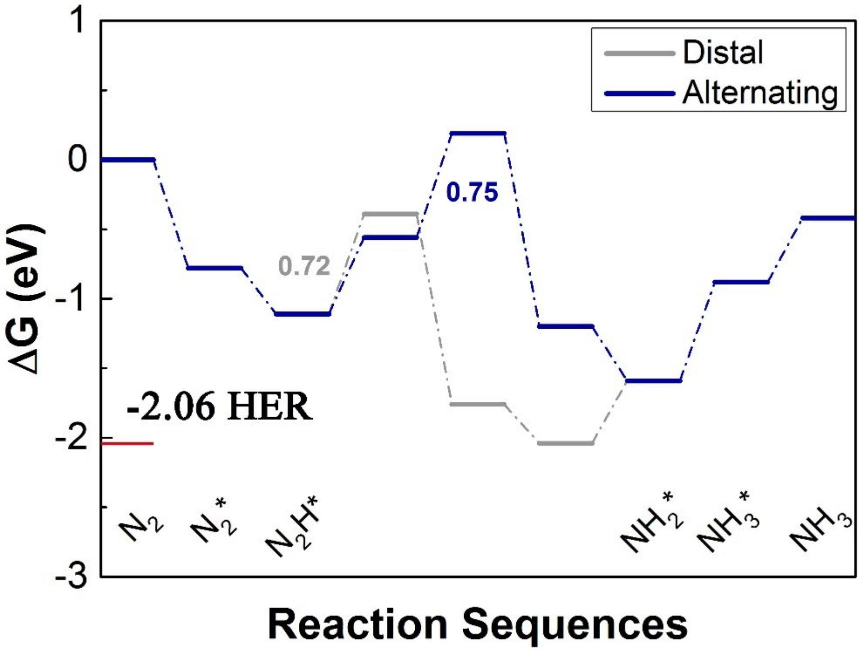

Figure S13. Gibbs free energy of the N_2-fixation process of C1.

Reference

1. G. Kresse and D. Joubert, *Phys. Rev. B*, 1999, **59**, 1758-1775.
2. J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865-3868.
3. L. M. Azofra, N. Li, D. R. MacFarlane and C. Sun, *Energy Environ. Sci.*, 2016, **9**, 2545-2549.
4. W. R. Zhao, J. Zhang, X. Zhu, M. Zhang, J. Tang, M. Tan and Y. Wang, *Applied Catalysis B-Environmental*, 2014, **144**, 468-477.