Supporting information:

N_2 plasma assisted surface modification of g-C_3N_4 nanosheets for enhanced photocatalytic H_2O_2 production

Lei Li,[a] Tianwei Li,[a] Rui Ke,[b] Hong Tao,[a] Tingmin Di*[a] and Hongyang Zhao*[a]

[a] *Hubei Key Laboratory of Plasma Chemistry and Advanced Materials, School of Materials Science and Engineering, Wuhan Institute of Technology, Wuhan 430205, P. R. China.* Email: ditingmin19@wit.edu.cn, zhaohy@wit.edu.cn.

[b] Hubei Key Laboratory of Radiation Chemistry and Functional Materials, School of Nuclear Technology and Chemistry & Biology, Hubei University of Science and Technology, Xianning 437100, China.

1. Photocatalytic H_2O_2 production experiment

The photocatalytic experiment was carried out in a 100 mL flat-bottomed three-neck flask. In detail, 20 mg of the prepared sample was dispersed to 60 mL deionized water or aqueous ethanol (10 vol.% ethanol) by ultrasonic. Photocatalytic H_2O_2 production was performed under a 300 W Xenon lamp at O_2-equilibrated condition for 60 mins. Before photoreaction, the system was purged with O_2 and stirred for 30 mins to reach the adsorption/desorption equilibrium of O_2. The light source was located at a distance of 10 cm from the reactor, and a continuous magnetic stirrer during the experiment. During illumination, 1 mL of solution was extracted every 15 min and a Millipore filter with a pore size of 0.22 μm was used to remove the photocatalyst. The amount of H_2O_2 was analyzed by iodometry. Generally, 200 μL of the solution obtained before was taken in a 5 mL brown centrifuge tube and then 800 μL deionized water, 1 mL potassium hydrogen phthalate ($C_8H_5KO_4$, 0.1 mol/L) aqueous solution, then 1 mL potassium iodide (KI, 0.4 mol/L) aqueous solution were sequentially added. After shaking well, the solution was let stand for 30 mins. In this process, H_2O_2 reacts with I^- forming I_3^-, which has a strong absorbance at 350 nm. Thus, UV-vis spectrometer was used to detect the concentration of I_3^-. Thus, the concentration of H_2O_2 was estimated according to the concentration of I_3^-.

The H_2O_2 evolution cycling tests were conducted under the same procedure of photocatalytic reactions. Then, the reacted photocatalyst in the cycle experiments was centrifuged and rinsed with deionized water for the next cycle. The degradation behavior of H_2O_2 over the as-synthesized photocatalysts was investigated by degrading 1 mmol L^{-1} H_2O_2 under 300 W xenon lamp irradiation.

2. Characterization

A Rigaku X-ray diffractometer (Japan) with Cu Ka radiation was used to test X-ray diffraction (XRD) patterns. Morphological observations were conducted on a JEOL JSM-7500 field emission scanning electron microscope (FESEM, Japan). UV–vis diffuse reflectance spectra were analyzed on a Shimadzu UV-3600 UV–vis spectrophotometer (Japan). The Brunauer–Emmett–Teller (BET) specific surface area

(S_{BET}) and CO_2 adsorption of the powders were measured on a Micromeritics ASAP 3020 with nitrogen and carbon dioxide adsorption apparatus (USA), respectively. X-ray photoelectron spectroscopy (XPS) was performed on a Thermo Scientific K-Alpha XPS spectrometer system with Al Ka (1486.6 eV) radiation. The binding energies were referenced to the C1s peak at 284.8 eV from adventitious carbon. The content of N element was measured on an ONH836 oxygen nitrogen hydrogen analyzer (LECO, USA). Photoluminescence (PL) spectra of the samples were analyzed by a fluorescence spectrophotometer (FluoroMax-4, HORIBA Scientific, Japan). The time-resolved photoluminescence (TRPL) spectra were obtained from a fluorescence lifetime spectrophotometer (FLS 1000, Edinburgh, UK). The Bruker EMXplus-6/1 model spectrometer was employed to obtain the electron paramagnetic resonance (EPR) spectra.

3. Photoelectrochemical measurements

Electrochemical measurements were measured on an electrochemical workstation (CHI660C, China) in a standard three-electrode system. The photoelectrodes were prepared as follows. 20 mg powder sample was dispersed into 20 uL Nafion and 300 uL of ethanol under ultrasonication for 30 min. The as-prepared samples coated on a FTO glass acted as the working electrode with an active area of ca.1.0 cm^2, whereas a Pt wire and Ag/AgCl (saturated KCl) were used as the counter and reference electrode respectively. 50 mL 0.5 M Na_2SO_4 aqueous solution was selected as the electrolyte.

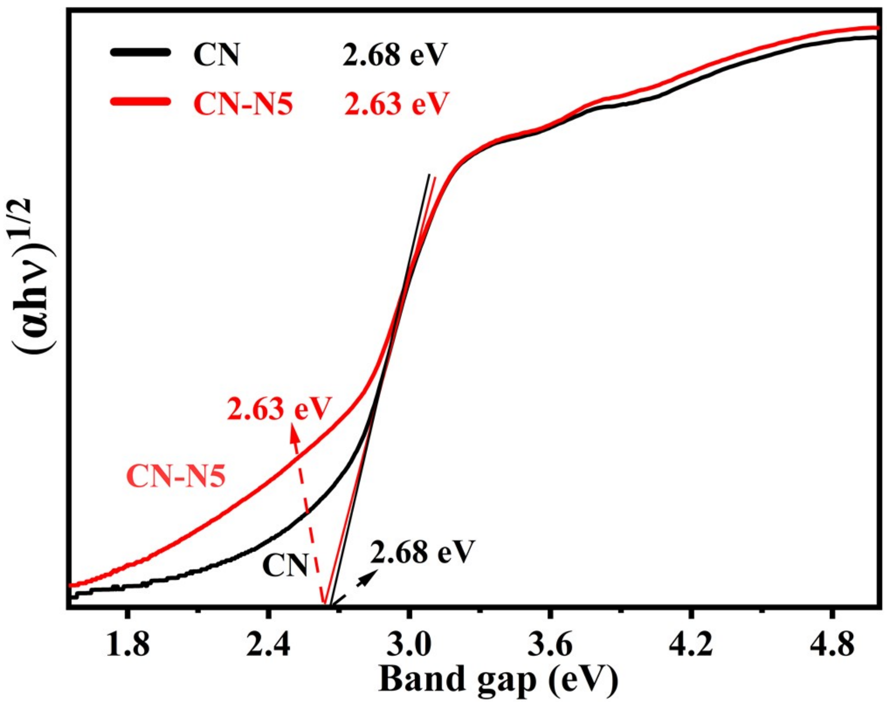

Fig. S1 The Tauc plots of CN and CN-N5.

Table S1. The bonding status and ratios of bonds in CN and CN-N5 samples

Bonding status/ ratio （%）	C 1s spectra （eV）			N 1s spectra （eV）			O 1s spectra （eV）	
	$C_{C–C}$ 284.6	$C_{C=O}$ 286.3	$C_{N–C=N}$ 288.1	$N_{C–N=C}$ 398.4	$N_{N–(C)3}$ 399.9	$N_{C–N–H}$ 401	$O_{O–C}$ 531.9	$O_{–OH}$ 533.2
CN	42.1	3.7	54.2	71.8	20.5	7.7	62.2	37.8
CN-N5	20.9	6.3	72.8	79.6	11.5	8.9	73.7	26.3

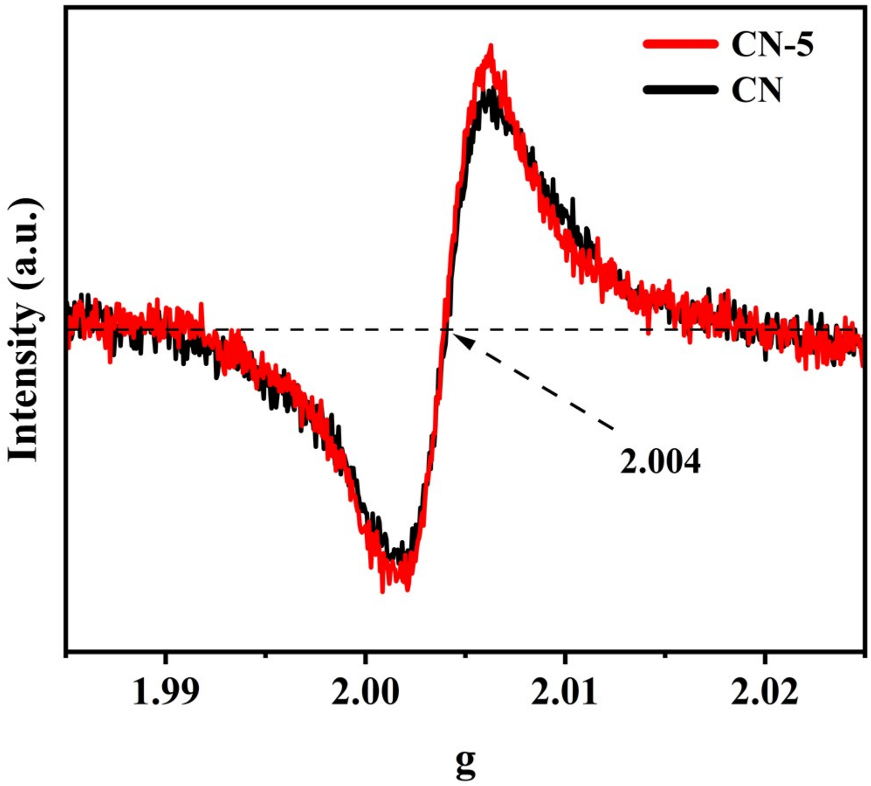

Fig. S2 The EPR spectra of CN and CN-N5.

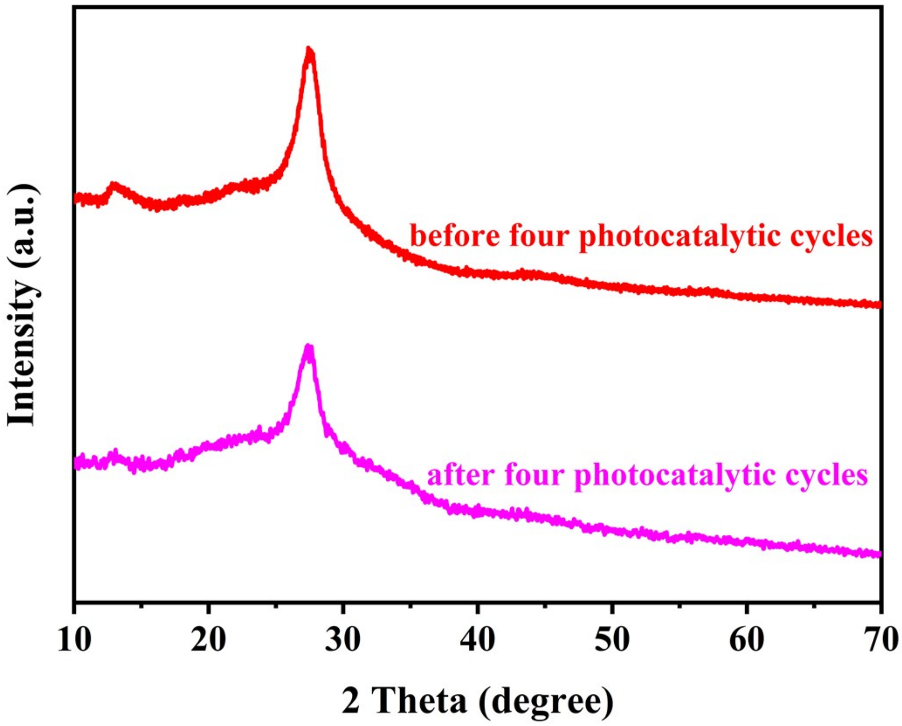

Fig. S3 The XRD patterns of CN-N5 before and after four consecutive photocatalytic cycles.

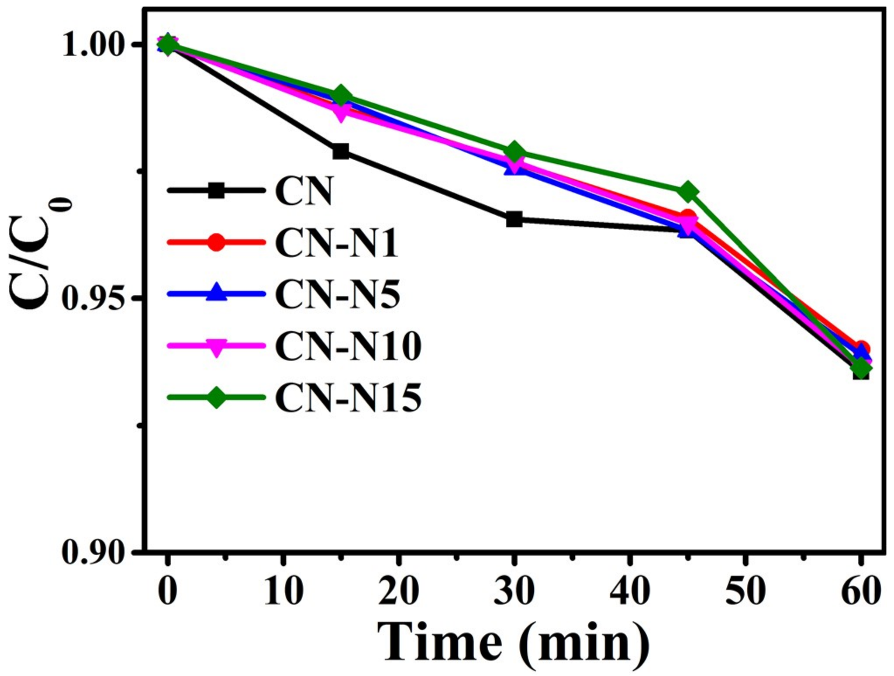

Fig. S4. Time-dependent H_2O_2 decomposition curves of the g-C_3N_4 before and after N_2 plasma treatment under Xe lamp irradiation (initial concentration of H_2O_2: 1 mmol/L).

Calculation of lifetime of the photogenerated carrier. The decay curves obtained from TRPL can be well fitted by the following three-exponential equation:

$$I_t = I_0 + A_1\exp(-t/\tau_1) + A_2\exp(-t/{}^{\tau}3) + A_3\exp(-t/{}^{\tau}3) \qquad \text{(S1)}$$

Where the I_0 represents the baseline correction value, A_1, A_2, and A_3 and are the preexponential factors, and τ_1, τ_2 represent the lifetime of the radiant energy transfer process (ns), while τ_3 represents the lifetime of the non-radiative energy transfer process (ns). The average lifetime (τ_{ave}) can be calculated according to the following equation:

$$\tau_{ave=}(A_1\tau_1^2 + A_2\tau_2^2 + A_3\tau_3^2)_/(A_1\tau_1 + A_2\tau_2 + A_3\tau_3) \qquad \text{(S2)}$$

Table S2. τ_{ave} of CN and CN-N5 fitted by triple exponential fitting

sample	τ_1 (ns)	A_1 (%)	τ_2 (ns)	A_2 (%)	τ_3 (ns)	A_3 (%)	τ_{ave} (ns)
CN	2.06	28.03	7.11	44.53	34.13	27.45	26.20
CN-N5	2.00	30.73	6.98	43.89	34.07	25.38	25.74