

## Supporting Information

### Switching the Photocatalytic Activity of g-C<sub>3</sub>N<sub>4</sub> by Homogenous Surface Chemical Modification with Nitrogen Residues and Vacancies

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#### Section S1: Experimental methods:

**Synthesis of CN.** Typically, 2 g of dicyandiamide powder was put into a covered crucible and then heated at a rate of 5 °C min<sup>-1</sup> to reach the temperature of 550 °C and maintained at this temperature in air for 2 h.

**Synthesis of CN-x.** 600 mg of CN powder was suspended into 20 mL of DMF solution in a 50 mL Teflon-lined autoclave and sonicated for 10 min. Then, k mL 80% hydrazine hydrate aqueous solution (k = 0.05, 0.1, 0.25, 0.4, 0.5) was added into the above autoclave and sonicated for another 30 min. Later, the autoclave was put into an oven at 150 °C for 2 h. After the reaction, the products were washed with deionized water by the centrifugation methods and dried at 80 °C under vacuum for 24 h.

**Synthesis of CN-x-H.** The hydrogen-treated CN-x (CN-x-H) was obtained by annealing CN-x in hydrogen atmosphere (X) at 400 °C for 2 h in a tube furnace.

**Characterization.** The structures of the power samples were investigated by X-ray diffractometer (XRD, Bruker D8 Advanced Diffractometer operating with Cu K $\alpha$  radiation). The angular range was  $2\theta = 5-75^\circ$ , with a speed of 6 °/min. Infrared transmission was obtained with a Fourier transform infrared (FTIR) spectrophotometer Spectrum (Nicolet). The optical absorbance spectra of the samples were performed on using a UV-vis spectrometer (CARY 300). All binding energies were referenced to C1s peaks (284.8 eV) arising from surface hydrocarbons (or possible adventitious hydrocarbon). Element analysis was conducted by an elemental analyzer (vario EL II; Elementar Analysensysteme, Germany). The photoluminescence measurements were performed in an Edinburgh instruments (FLSP 920) system operated at room temperature. Electron paramagnetic resonance (EPR) measurements were operated at EMX-8/2.7. Surface binding elements were analyzed with X-ray photoelectron spectroscopy (XPS, USA

Thermo ESCALAB 250). All binding energies were referenced to C1s peaks (284.8 eV) arising from surface hydrocarbons (or possible adventitious hydrocarbon). Prior peak deconvolution, X-ray satellites, and inelastic background (Shirley-type) were subtracted for all spectra. The carbon K-edge X-ray absorption near-edge structure (XANES) measurement of the samples were performed at the beamline 4B7B of Beijing Synchrotron Radiation Facility (BSRF). Transmission electron microscopy (TEM, JEM 2100, 200 kV) were used to characterize the morphology and structure of the obtained products.

**Photocatalytic test.** The photocatalytic reaction was performed in a pyrex glass cell connected to a glass closed gas circulation system. The deposition of 3 wt% Pt was conducted by directly immersing the products into  $\text{H}_2\text{PtCl}_6$  ethanol solution and calcinated at 180 °C for 30 min (ramp: 2 °C min<sup>-1</sup>).  $\text{H}_2$  evolution analysis was performed by dispersing 50 mg of catalyst powder in an aqueous solution containing triethanolamine (100 mL, 10 vol. %) as the sacrificial electron donor. The reactant solution was evacuated several times to remove air completely before the reaction. A 300 W Xe lamp with a 420 nm cutoff filter was used as the light source. A flow of cooling water was used during the reaction to maintain the temperature of the reactant solution at 15 °C. The amount of evolved  $\text{H}_2$  evolved was analyzed by gas chromatography (TECHCOMP, 7890 II).

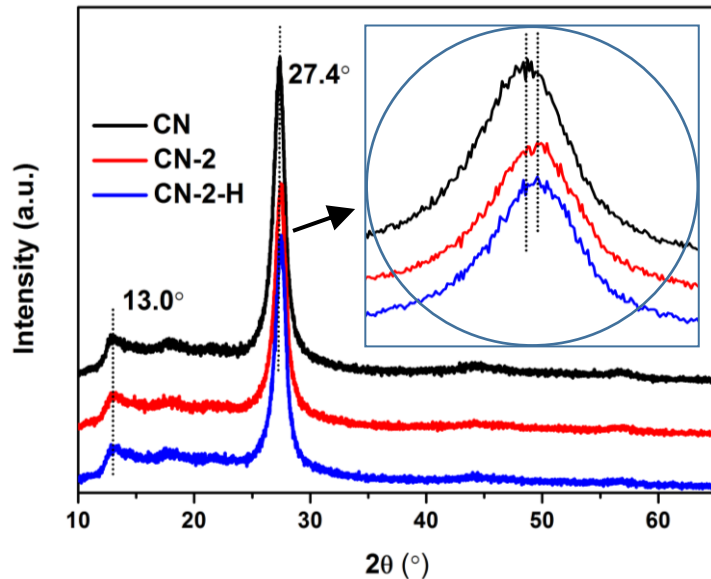
**Photoelectrochemical Measurements.** Photocurrent was conducted with an electrochemical analyzer (CHI660E Instruments) in a standard three-electrode system using the prepared samples as the working electrodes, using a Pt gauze electrode and Ag/AgCl (saturated KCl) as the counter electrode and reference electrode, respectively. The working electrodes were immersed in the electrolyte (0.2 M  $\text{Na}_2\text{SO}_4$  aqueous solution) for 60 s before any measurements were taken.

The working electrode was prepared on fluoride tin oxide (FTO) conductor glass, which was cleaned by sonication in acetone and ethanol for 10 min each. 10 mg of powder was mixed with 0.2 mL DMF and 0.05 mL Liquion solution to make a slurry. The slurry was then injected onto the FTO glass, whose sides were previously covered with Scotch tape and the exposed area of electrodes was 0.785 cm<sup>2</sup>. These electrodes were dried at 120 °C for 30 min in air to improve adhesion.

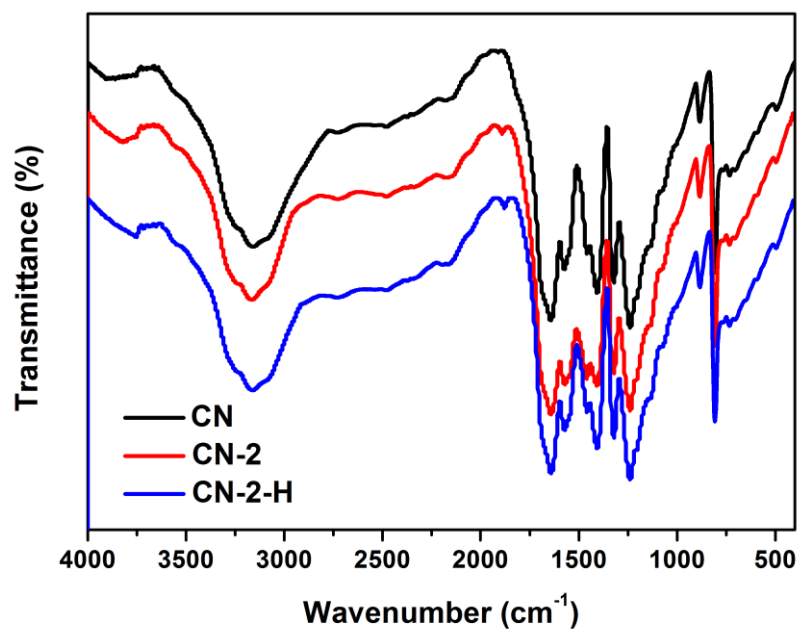
## Section S2: Crystal and chemical structures.

Sample	C (%)	N (%)	H (%)	Others (%)	C/N (atomic)
CN	34.63	60.57	1.98	2.82	0.6670
CN-1	34.66	60.69	2.00	2.65	0.6663
CN-2	34.63	60.70	2.02	2.65	0.6655
CN-3	34.59	60.71	2.02	2.68	0.6648
CN-4	34.45	60.75	2.23	2.57	0.6615
CN-5	34.32	60.83	2.30	2.55	0.6582
CN-H	34.59	60.43	2.05	2.93	0.6678
CN-1-H	34.64	60.46	2.09	2.81	0.6684
CN-2-H	34.62	60.40	2.09	2.9	0.6687
CN-3-H	34.60	60.37	2.11	2.92	0.6687
CN-4-H	34.60	60.29	2.18	2.93	0.6696
CN-5-H	34.35	59.64	2.21	3.80	0.6720

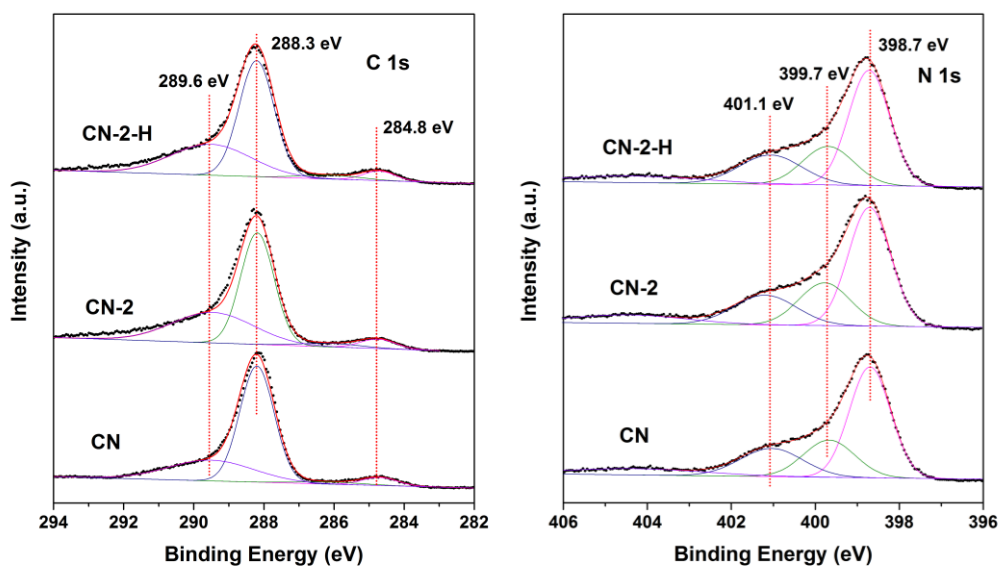
**Table S1.** The results of elemental analysis for the CN, CN-x and CN-x-H samples.



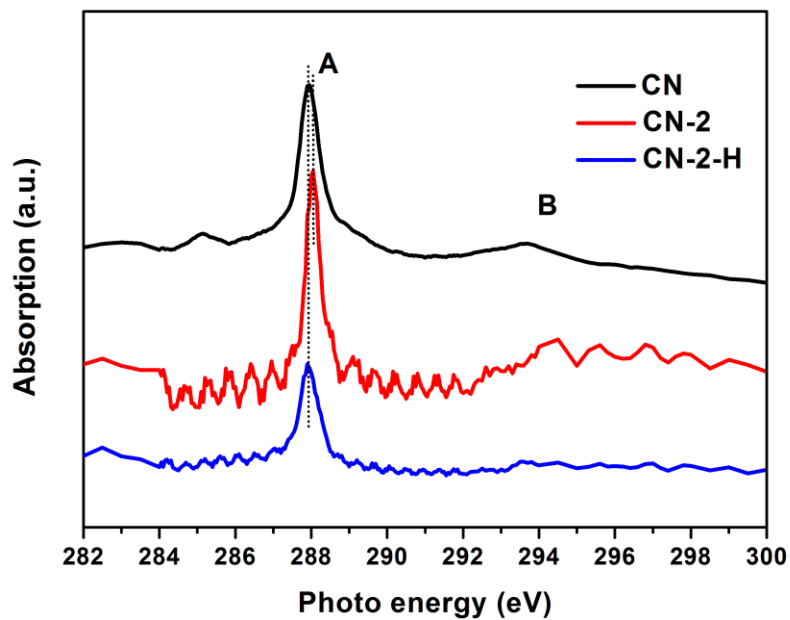
**Figure S1.** XRD patterns of as-prepared CN, CN-2 and CN-2-H samples.



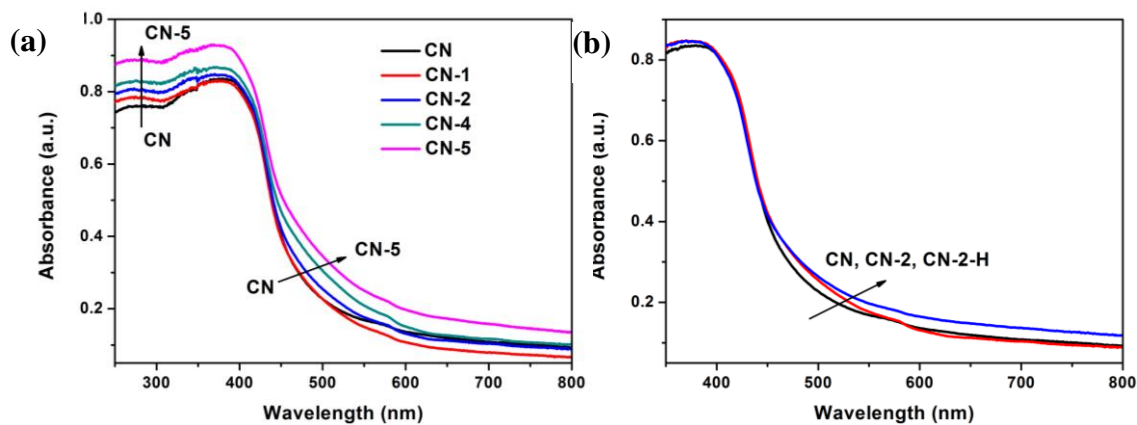
**Figure S2.** FTIR spectra of as-prepared CN, CN-2 and CN-2-H samples.



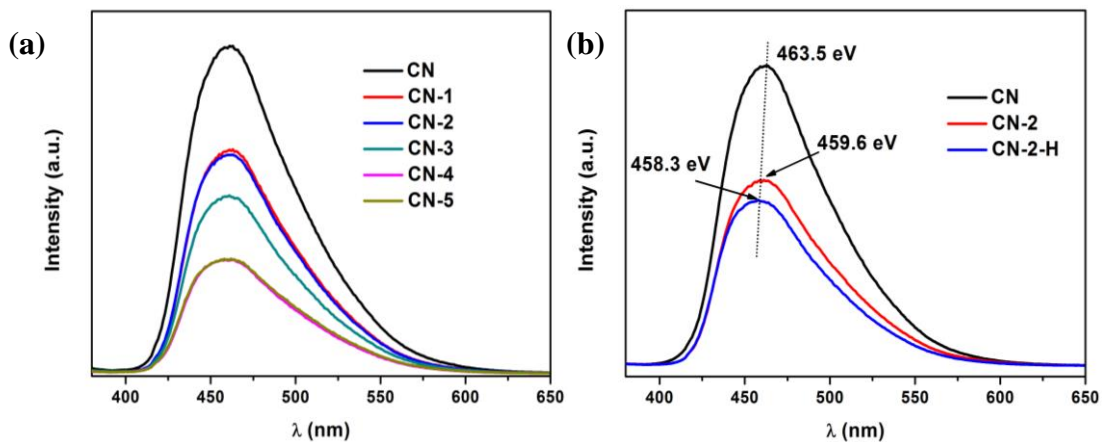
**Figure S3.** C 1s and N 1s XPS spectra of pristine CN, CN-2 and CN-2-H.



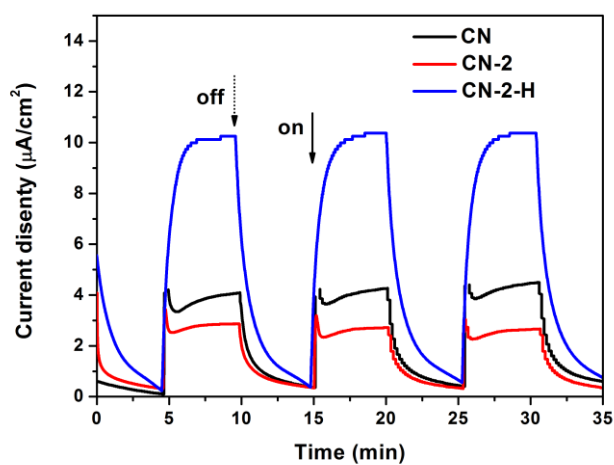
**Figure S4.** Comparison of C K-edge XANES spectra of CN, CN-2 and CN-2-H samples.



**Figure S5.** UV-vis absorption spectra of (a) CN and CN-x samples, (b) CN, CN-2 and CN-2-H samples.



**Figure S6.** Room temperature PL spectra for (a) pristine CN and CN-x samples, and (b) pristine CN, CN-2 and CN-2-H.



**Figure S7.** Transient photocurrent density versus time plotted for CN, CN-2 and CN-2-H samples at 0.6 V vs Ag/AgCl in 0.2 M  $\text{Na}_2\text{SO}_4$  electrolyte under simulated sunlight irradiation.