

## Electronic Supplementary Information(ESI)

### Etching-induced highly porous polymeric carbon nitride with enhanced photocatalytic water splitting

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### Experimental section

#### 1. Materials

All the chemical reagents are analytical pure and used as received without further purification.

#### 2. Preparation of porous polymeric carbon nitride

The photocatalysts were synthesized by a calcination method. First, a certain volume of concentrated sulfuric acid was added to 10 mL of cyanamide aqueous solution, followed by ultrasonic dispersion for 1 min. Then, the mixed solution was transferred to a crucible and calcinated in a muffle furnace at 550°C for 4 h. Finally, the powder was ground to obtain the final product.

According to the volume ratio of CY to H<sub>2</sub>SO<sub>4</sub>, the obtained samples were denoted as CN-0.2H, CN-0.25H, and CN-0.35H, respectively. As a comparison, the original carbon nitride was prepared by directly placing 10 mL of cyanamide aqueous solution in a crucible and calcination in a muffle furnace at 550°C for 4 h.

#### 3. Characterization

X-ray powder diffractometer (XRD, Rigaku D/MAX2200-PC) was used to analyze the crystallinity and crystal structure of the product. Test conditions: Cu K $\alpha$  rays,  $\lambda$  = 0.15418 nm, scanning speed 5°/min, scan range 10°-80°. The morphology of samples

was characterized by TEM(JEM-100CXII) and HRTEM (JEOL-2010) with an accelerating voltage of 200 kV. The EDS mapping was obtained through FE-SEM (SU-8010, Hitachi). Fourier transform infrared spectroscopy (FT-IR Bruker Alpha) adopt the KBr tablet method, and the measurement range was set from 400 to 4000  $\text{cm}^{-1}$ . The UV-Vis absorption spectrum (UV-Vis, Agilent Cary Series UV-Vis spectrometer) of the samples are tested with  $\text{BaSO}_4$  as the background. Room temperature photoluminescence spectra (PL, Agilent Cary Eclipse) and room temperature phosphorescence spectra were obtained by a fluorescence/phosphorescence spectrophotometer to characterize the electron-hole pair recombination rate of the sample. In the phosphorescence lifetime test (Edinburgh FLS920), the excitation of 370 nm laser was adopted, and the time-correlated single-photon counting technique (TCSPC) was used to record the fluorescence decay process. Solid-state  $^{13}\text{C}$  nuclear magnetic resonance (NMR) spectra were tested on an AV 400M spectrometer (Bruker, Germany). The X-ray photoelectron spectroscopy (XPS) tests were performed on a Thermo Scientific Escalab 250 Xi spectrometer with Al  $K\alpha$  radiation ( $h\nu = 1486.6$  eV) to detect the chemical states of elements in the samples. The binding energy reference was taken at 284.8 eV for the C 1s peak arising from surface hydrocarbons. The electron spin resonance signal (ESR) was measured to analyze the single electrons in the molecular orbital of a substance by using the JES-X320 spectrometer.

#### **4. Photoelectrochemical measurements**

Electrochemical impedance spectroscopy (EIS) and Mott-Schottky curve were tested on an electrochemical workstation (Shanghai Chenhua, CHI 660E) using a standard three-electrode electrolytic cell. The Pt nanoplate and Ag/AgCl were employed as the counter electrode and the reference electrode, respectively. The working electrode was prepared by the drop coating method. First, the sample was dispersed in a mixed solution of Nafion and water, and then was coated onto a 2 cm $\times$ 1 cm clean FTO glass, and finally dried at 60 $^\circ\text{C}$  for 24 h, followed by calcination at 200 $^\circ\text{C}$  for 2 h under  $\text{N}_2$  atmosphere. A 300 W xenon arc lamp (CEL-HXF300) with a filter (AM 1.5G, Ceaulight) was used to simulate solar illumination with  $\sim 1$  sun power. The EIS measurement was performed at 1.0 V versus RHE, using a 10 mV amplitude

perturbation from 0.1 MHz to 0.01 Hz under 1 sun illumination, while Mott-Schottky plots were measured at a frequency of 1 kHz under dark.

The value of  $J_{\text{abs}}$  is calculated according to the following equations.

$$J_{\text{abs}} = \frac{q}{hc} \int \lambda \phi_{\lambda} \eta_{\text{abs}} d\lambda$$

$$\eta_{\text{abs}} = (1 - 10^{-A}) \times 100\%$$

The  $J_{\text{abs}}$  is the photon adsorption rate expressed as the photocurrent density, and the  $q$  is the charge of an electron,  $h$  is the Plank constant,  $c$  is the light speed,  $\phi_{\lambda}$  is the photon flux of the AM 1.5G solar spectrum, and  $\eta_{\text{abc}}$  is the light absorption efficiency.

## 5. Photocatalytic H<sub>2</sub> evolution tests

For every photocatalytic hydrogen production test, 0.02 g of the photocatalyst was added into a reaction cell containing 80 mL of 10 vol % triethanolamine (TEOA) aqueous solution, and the mixture was sonicated for 5 min. Then, the cell was vacuumized after adding 1 g L<sup>-1</sup> H<sub>2</sub>PtCl<sub>6</sub> solution into the dispersion with a Pt/photocatalyst ratio of 3 wt %. Photodeposition of Pt on the photocatalyst was first completed by irradiation for 1 h using a CEL-HXF300 Xe lamp (300 W, Ceaulight). Then, the cell was placed under a vacuum again. The hydrogen evolution reaction was started by irradiation using the Xe lamp equipped with a CEL-S500 AM 1.5G filter (100 mW cm<sup>-2</sup>). Gas chromatography with the carrier gas of N<sub>2</sub> (TCD, GC-7920, Ceaulight) was used to analyze the generated hydrogen.

In the apparent quantum efficiency (AQY) test, single wavelength filters of 400, 420, 450, 480, 500, 520, 540, 560, 580, and 600 nm were employed with illumination intensities of 0.82, 1.37, 1.91, 2.65, 2.08, 1.37, 2.04, 2.08, 2.13 and 2.15 mW/cm<sup>2</sup>, respectively. The value of AQY was calculated according to the following equation,

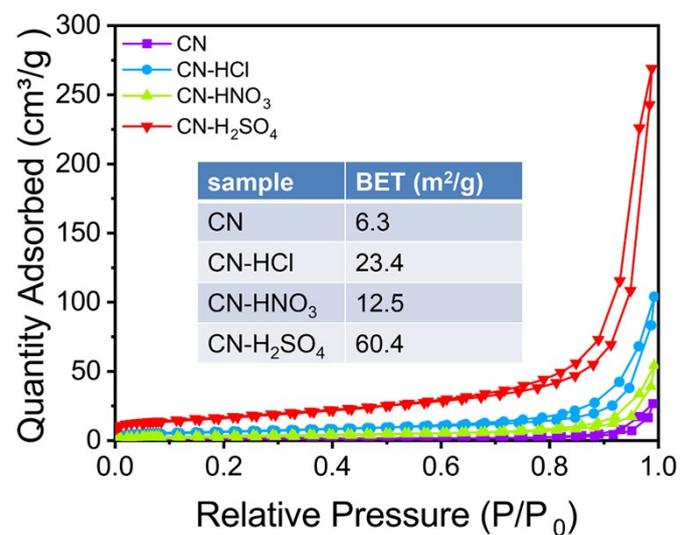
$$AQY (\%) = \frac{N_e}{N_p} \times 100\% = \frac{2 \times M \times N_A \times h \times c}{P S t \lambda_i} \times 100\%$$

Where  $N_e$  was the number of reacted electrons,  $N_p$  was the number of incident photons,  $M$  was the molar amount of hydrogen molecules,  $N_A$  was the Avogadro constant,  $h$

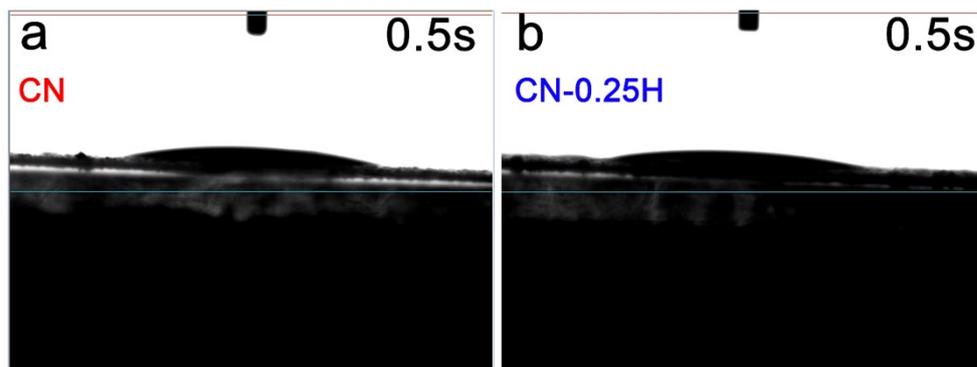
was the Planck constant,  $c$  was the speed of light under vacuum,  $P$  corresponded to the incident power, and  $S$  was the irradiation area of the photocatalytic reactor ( $3.46\text{cm}^2$ ),  $t$  was the photoreaction time ( $3600\text{s}$ ), and  $\lambda_i$  was the wavelength of monochromatic light.

## **6. Theoretical calculation**

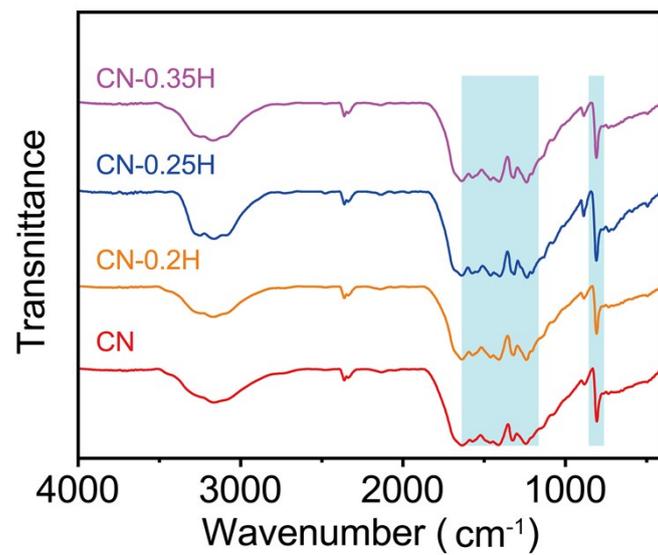
To better understand the electronic structure changes in CN- $x$ H, spin-polarized density functional theory calculations were carried out with the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional and projector-augmented wave (PAW) pseudopotentials as implemented in the Vienna ab initio simulation package (VASP). The wave functions were expanded in a plane wave basis with an energy cutoff of  $500\text{ eV}$ . The gamma centered scheme K-points grid sampling was set at  $\Gamma$  point for all the calculations. The van der Waals (vdW) interactions were involved, which were corrected by the DFT-D3 approach, and all the structural relaxations were carried out until the residual forces were below  $0.02\text{ eV \AA}^{-1}$ . To obtain exact band gaps of CN and CN- $x$ H, Heyd-Scuseria-Ernzerhof (HSE) hybrid functional with  $\omega$  equaled to  $0.2\text{ \AA}^{-1}$  was employed.



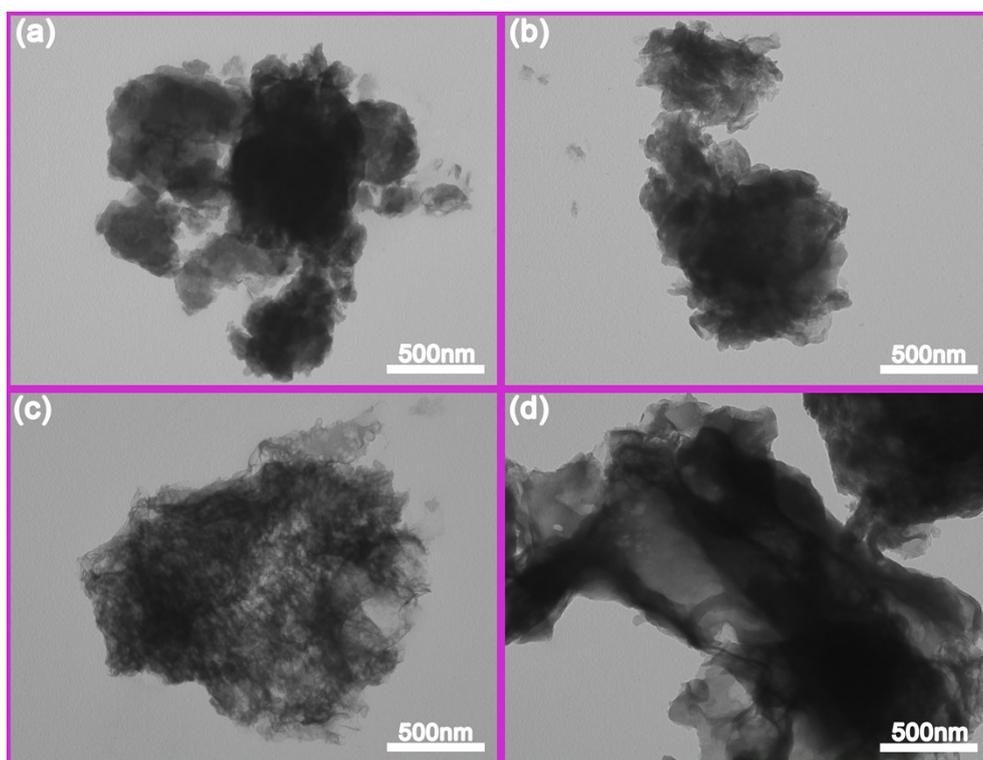
**Figure S1.** Surface areas of polymeric CN with various inorganic acids.



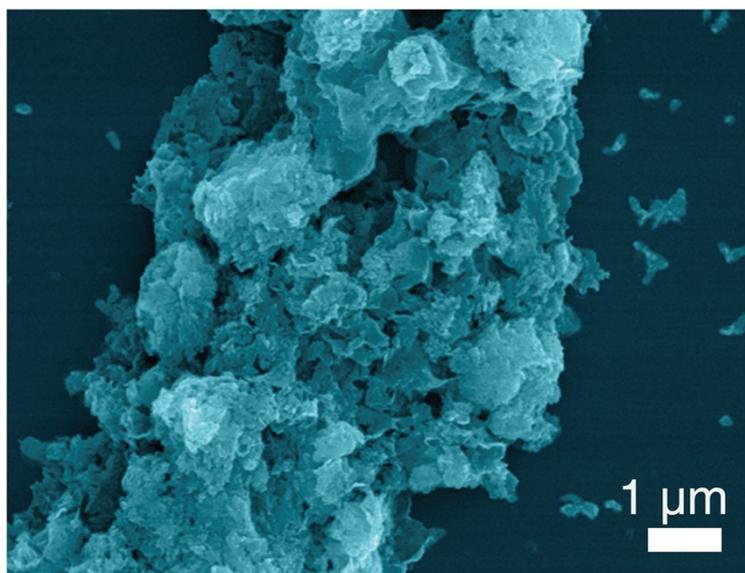
**Figure S2.** Optical images of water spreading on the surface of CN and CN-0.25H.



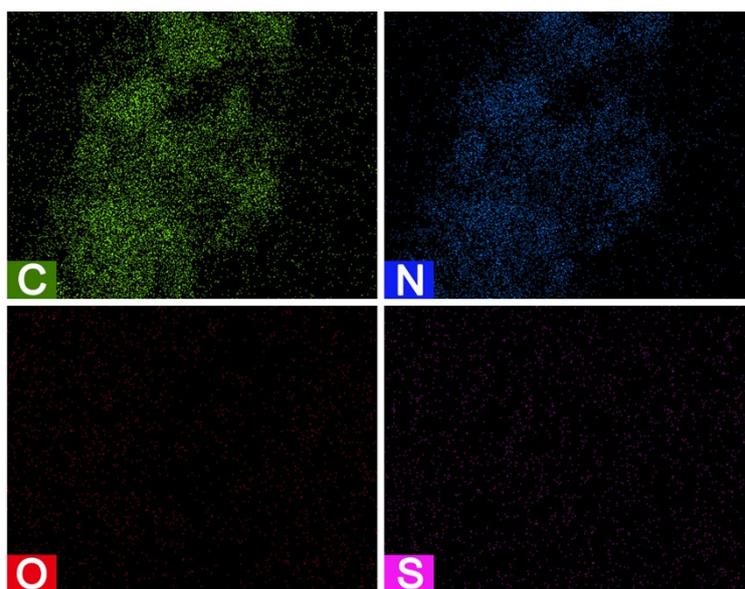
**Figure S3.** FT-IR spectrum.



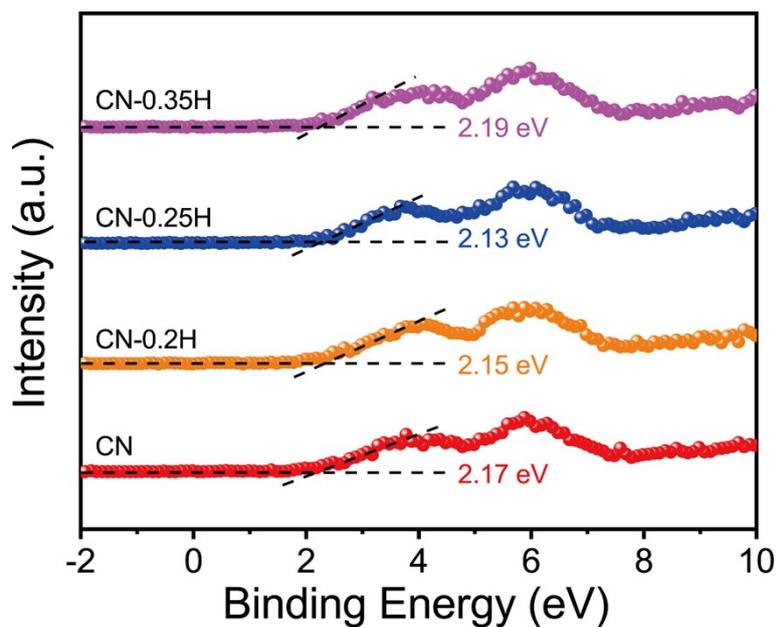
**Figure S4.** TEM images for CN, CN-0.2H, CN-0.25H, and CN-0.35H.



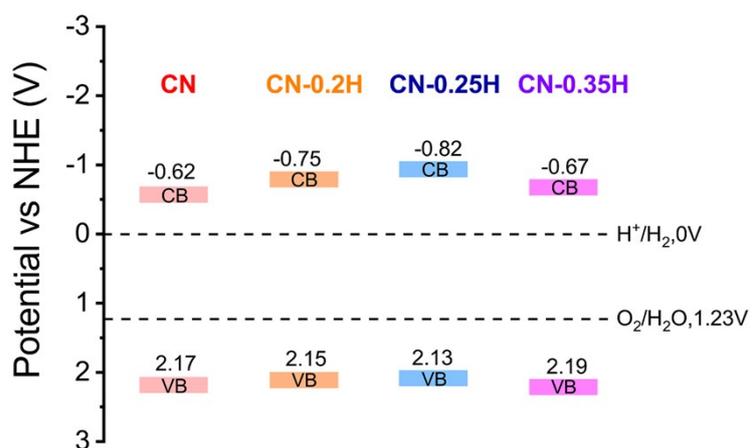
**Figure S5.** SEM image of CN-0.25H.



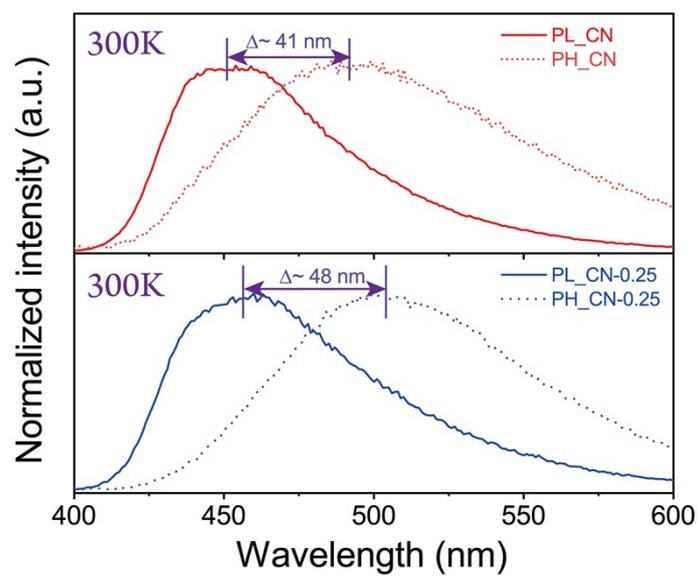
**Figure S6.** EDS elemental mapping of CN-0.25H.



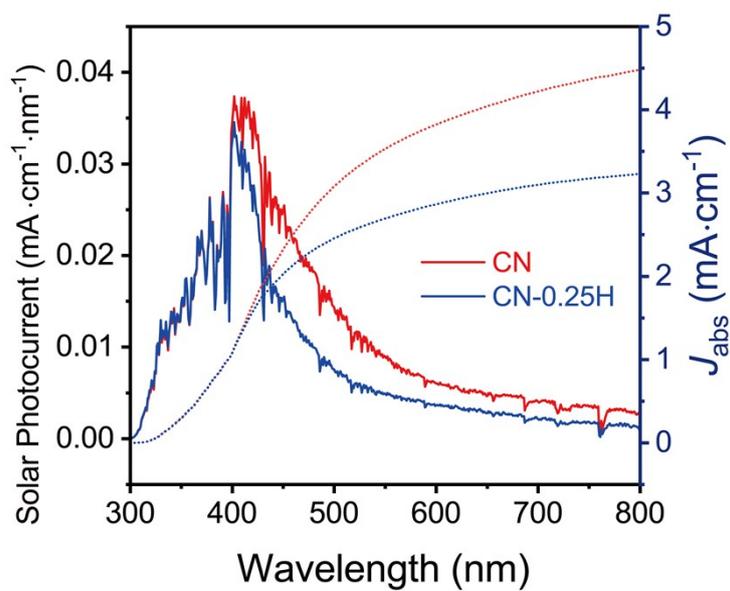
**Figure S7.** Valence-band XPS spectra of CN and CN-xH.



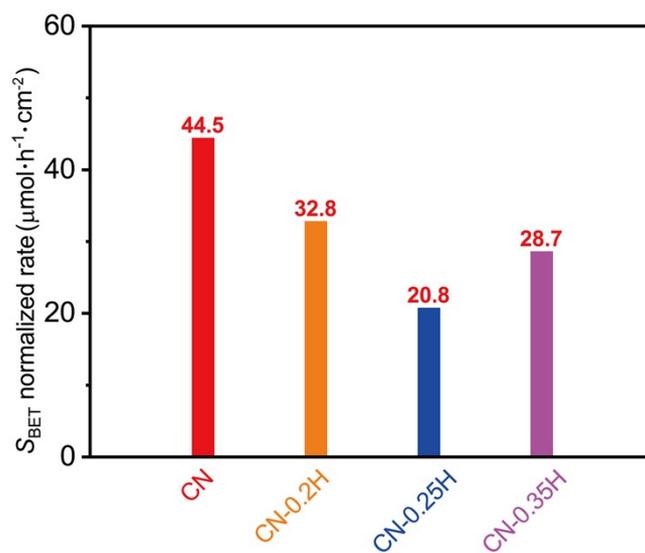
**Figure S8.** The energy band diagrams.



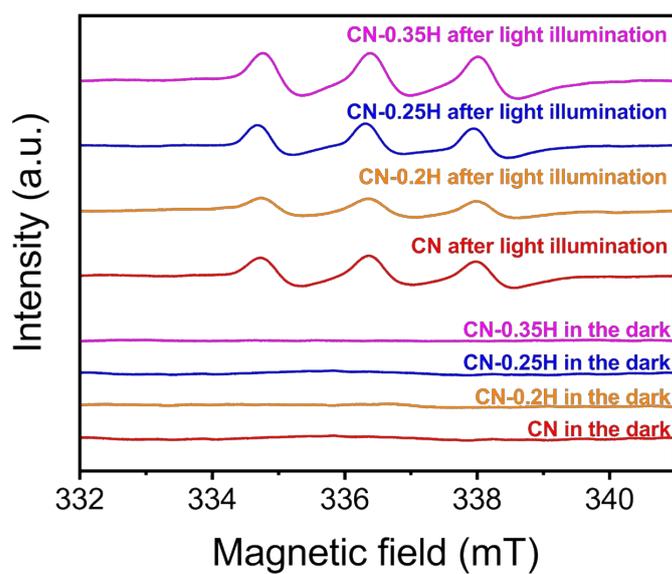
**Figure S9.** Normalized steady-state PL and phosphorescence (PH) measurements.



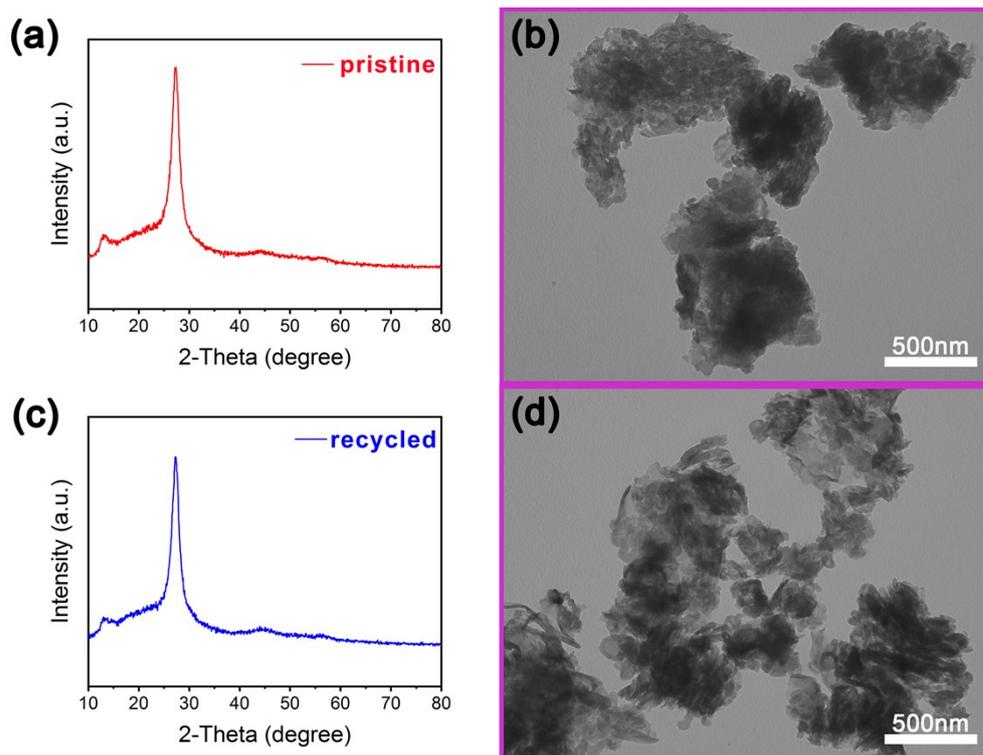
**Figure S10.** The photon absorption rates ( $J_{\text{abs}}$ ) of CN and CN-0.25H.



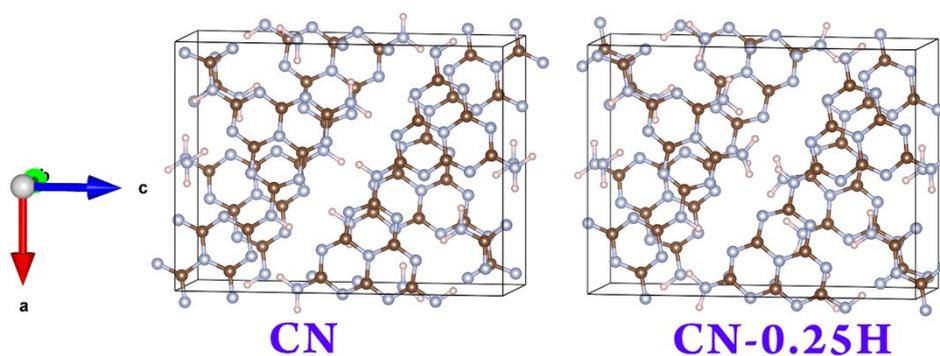
**Figure S11.**  $S_{\text{BET}}$  normalized hydrogen production rate.



**Figure S12.** TEMP spin-trapped  $^1\text{O}_2$  spectra.



**Figure S13.** XRD pattern and TEM image of recycled CN-0.25H with an evacuation time of 4 h.

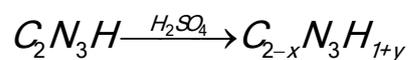


**Figure S14.** The optimized geometries of CN and CN-0.25H.

**Table S1.** The elemental analysis for CN and CN-xH.

samples	N(%)	C(%)	H(%)	C/N
CN	59.12	33.48	2.239	0.566
CN-0.2H	57.9	32.04	2.486	0.553
CN-0.25H	55.85	30.70	2.511	0.550
CN-0.35H	55.28	30.28	2.567	0.548
CN-0.5H	53.34	28.7	2.898	0.538

According to the theoretical atomic ratio and elemental analysis for polymeric carbon nitride, the reaction formula for the etching process to prepare porous polymeric carbon nitride is written as follows:



**Table S2.** AQY of CN-0.25H compared with other up-to-date CNs and their compositions.

Photocatalyst	AQY(%)	Experimental conditions	Ref.
HCNS	7.5@420nm	3 wt%Pt,10 vol.% TEOA	1
a-CN	6.1@420nm	100mg,1 wt%Pt,10 vol.% TEOA	2
DCNS	4.7@420nm	50mg,3 wt%Pt,10 vol.% TEOA	3
Melamine and glucose	5@420nm	30 mg samples, 3 wt% Pt-loading	4
Pt/C-rich/g-C <sub>3</sub> N <sub>4</sub>	4.52@420nm	10mg,3 wt%Pt,10 vol.% TEOA	5
1.0 wt% Pt/g-C <sub>3</sub> N <sub>4</sub>	3.96@420nm	10mg ,10 vol.% TEOA	6
Incorporation of C=C into ultrathin g-C <sub>3</sub> N <sub>4</sub>	4.8@420nm	50mg,3 wt%Pt,10 vol.% TEOA	7
S-doped g-C <sub>3</sub> N <sub>4</sub>	3.9@420nm	40 mg,1 wt% Pt,10 vol.% TEOA	8
GQDs/g-C <sub>3</sub> N <sub>4</sub>	5.25@420nm	20mg,3 wt%Pt,10 vol.% TEOA	9
P-TCN	5.7@420nm	100mg,1 wt% Pt,10 vol%Methanol	10
Pdots/g-C <sub>3</sub> N <sub>4</sub> nanosheets	5.7@420nm	10 vol % TEOA	11
<b>CN-0.25H</b>	<b>6.7@420nm</b>	<b>20mg,3wt%Pt,10vol%TEOA</b>	<b>This work</b>

## References

1. J. Sun, J. Zhang, M. Zhang, M. Antonietti, X. Fu and X. Wang, *Nat. Commun.*, 2012, **3**, 1139.
2. M. Z. Rahman, P. C. Tapping, T. W. Kee, R. Smernik, N. Spooner, J. Moffatt, Y. Tang, K. Davey and S.-Z. Qiao, *Adv. Funct. Mater.*, 2017, **27**, 1702384.
3. Q. Shen, N. Li, R. Bibi, N. Richard, M. Liu, J. Zhou and D. Jing, *Appl. Surf. Sci.*, 2020, **529**, 147104.
4. W. Che, W. Cheng, T. Yao, F. Tang, W. Liu, H. Su, Y. Huang, Q. Liu, J. Liu, F. Hu, Z. Pan, Z. Sun and S. Wei, *J. Am. Chem. Soc.*, 2017, **139**, 3021-3026.
5. Y. Li, M. Yang, Y. Xing, X. Liu, Y. Yang, X. Wang and S. Song, *Small*, 2017, **13**, 1701552.

6. W. Wang, Y. Tao, L. Du, Z. Wei, Z. Yan, W. K. Chan, Z. Lian, R. Zhu, D. L. Phillips and G. Li, *Appl. Catal. B-Environ.*, 2021, **282**, 119568.
7. H. Che, C. Li, P. Zhou, C. Liu, H. Dong and C. Li, *Appl. Surf. Sci.*, 2020, **505**, 144564.
8. H. Wang, Y. Bian, J. Hu and L. Dai, *Appl. Catal. B-Environ.*, 2018, **238**, 592-598.
9. J.-P. Zou, L.-C. Wang, J. Luo, Y.-C. Nie, Q.-J. Xing, X.-B. Luo, H.-M. Du, S.-L. Luo and S. L. Suib, *Appl. Catal. B-Environ.*, 2016, **193**, 103-109.
10. S. Guo, Z. Deng, M. Li, B. Jiang, C. Tian, Q. Pan and H. Fu, *Angew. Chem. Inter. Ed.*, 2016, **55**, 1830-1834.
11. W. Zhou, T. Jia, H. Shi, D. Yu, W. Hong and X. Chen, *J. Mater. Chem. A*, 2019, **7**, 303-311.