

Enhanced photocatalytic hydrogen production from aqueous-phase methanol reforming over cyano-carboxylic bifunctionally-modified carbon nitride

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Experimental Section

1. Materials

Melamine, dicyandiamide, trithiocyanuric acid, $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, NaCl, H_2SO_4 , methanol and benzyl alcohol were purchased from Sinopharm Chemical Reagent Co., Ltd, China. KSCN was purchased from Aladdin. All chemicals were used as received without further purification. The deionized water (18.2 M Ω cm) was homemade by a Fulham pure water machine.

2. Preparation of catalysts.

2.1 Bulk CN.

Melamine (10 g) was heated in a crucible using a muffle furnace at 550 °C for 4 h, with a ramp rate of 3 K min⁻¹ under ambient atmosphere. The light yellow product was ground thoroughly prior to characterization.

2.2 Cyano introduced CNS_x (x = 0.25, 0.05, 0.75 and 1.00).

A cyano group introduced sample was prepared by thermal treatment of the mixture of trithiocyanuric acid (TA) and melamine. Specifically, m g of trithiocyanuric acid (TA) and n g of melamine [$m + n = 10$ g, $x = m/(m+n)^{-1}$] were dissolved in ethanol and dried thoroughly to get a yellow block mixture. The mixture was heated through the above calcination procedure. Sample CNS_{1.00} also named as CNS.

2.3 CNS-H_y.

600 mg of the CNS sample was dispersed in a round-bottom flask which contain 100 mL of 3 M sulfuric acid aqueous solution. After that, the flask was heated in oil bath at 80 °C for 10 min, 1 h, 2 h and 4 h respectively. The resulting yellow mass was suspended in water and the insoluble product was isolated by centrifugation, washed with copious amount of water until the filtrate is neutral and dried at 60 °C in a vacuum oven.

2.4 Bulk g-C₃N₄ and Ribbon-like g-C₃N₄ in Table 1, entries 5 and 6.

As a typical procedure, dicyandiamide and NaCl with the mass ratio of 1:1 were mixed and ground to fine powders using a mortar and pestle. Then in nitrogen atmosphere, the fine powders were heated from room temperature to 600 °C at a rate of 19.3 °C min⁻¹ and kept at 600 °C for 60 min. After cooling to room temperature, 1 g obtained orange sample was grounded, then added into 100 mL deionized water and sonicated for 30 min. The dispersion was centrifuged at 4000 rpm for 10 min to obtain a homogenous dispersion. Then the dispersion was freeze-dried, and the target sample was finally obtained. The bulk g-C₃N₄ was prepared as a reference by heating dicyandiamide using the same heating procedure.¹

2.5 CN(KSCN) in Table 1, entry 8.

The synthetic method for CN are identical to the above bulk CN. KSCN treated CN was synthesized by thoroughly grounding CN (800 mg) with KSCN (1.6 g, dried at 140 °C in vacuum) and loaded in an alumina boat. In a tube furnace, this mixture was heated under argon to 400 °C at 30 °C min⁻¹ ramp for 1 h, and then to 500 °C at 30 °C min⁻¹ ramp for 30 min. The resulting yellow mass was suspended in water and the insoluble product was isolated by centrifugation, washed with copious amount of water and dried at 60 °C in a vacuum oven.²

2.6 CN-H, Ribbon-like g-C₃N₄-H and CN(KSCN)-H in Table 1, entries 2, 7 and 9.

600 mg of the respective samples were dispersed in a round-bottom flask which contain 100 mL of 3 M sulfuric acid aqueous solution. After that, the flask was heated in oil bath at 80 °C

for 2 h. The resulting yellow mass was suspended in water and the insoluble product was isolated by centrifugation, washed with copious amount of water until the filtrate is neutral and dried at 60 °C in a vacuum oven.

3. Photoactivity Measurements.

3.1 Hydrogen production reactions.

The hydrogen production reactions were conducted under N₂ atmosphere (1 atm) in a 500 mL Pyrex glass reactor with a sealed flange and a magnetic stirrer (Fig. S6). The suspensions were prepared by mixing H₂O (64 mL), methanol (36 mL), catalyst (50 mg) and H₂PtCl₆ (0.1 M, 260 μL) in a reactor equipped with a stirrer bar. The reactor were irradiated using a solar light simulator with a Xe lamp (300 mW cm⁻²) whilst stirring. The solar light simulator was equipped with an cut 420 nm filter to remove ultraviolet irradiation. The amount of accumulated H₂ was quantified via periodic injected 1 mL gas into a gas chromatograph (GC, Shimadzu GC-2014C, TCD detector) equipped with a 5 Å molecular sieve column (2 m × 3 mm). What's more, the amount of accumulated CO₂ was quantified via periodic injected 1 mL gas into a gas chromatograph (GC, Shimadzu GC-2014C, FID detector) (compared with a methane converter) equipped with a TDX-01 column (2 m × 3 mm). The temperature of the GC oven was maintained at 60 °C and N₂ was used as the carrier gas.

3.2 Benzyl alcohol oxidation.

The benzyl alcohol oxidation reactions were conducted under O₂ atmosphere (1 atm) in a 10 mL round-bottomed Pyrex glass flask with a sealed spigot and a magnetic stirrer (Fig. S11). The suspensions were prepared by mixing benzyl alcohol (0.2 mmol), acetonitrile (2 mL), catalyst (10 mg) in a reactor equipped with a stirrer bar. The reactor was irradiated using a white LED light (400 mW cm⁻²) whilst stirring at 60 °C. The benzyl alcohol oxidation products compositions were analyzed and determined by means of an Shimadzu GC-2014C gas chromatograph equipped with a WondaCAP column (30m × 0.25 mm, 0.25 μm) and a flame ionization detector (FID). The products was also identified by mass spectrometry (GC-MS, Agilent 6890N) coupled with 5973 Mass selective Detector.

4. Quantification methods.

The content of the gas products were calculated by using the external standard method. The area normalization method was used to determine the conversion of benzyl alcohol.

5. Characterization

5.1 XRD. Powder X-ray diffraction (XRD) spectroscopy (Fig. S1) was performed on a Bruker D8 Advanced diffractometer operating with Cu Kα1 radiation ($\lambda = 1.5405 \text{ \AA}$). The scan range was from 5 to 60° with the scan rate of 5° min⁻¹.

5.2 TEM and SEM. The morphology was operated using transmission electron microscopy (TEM, Tecnai G2 F20 S-Twin) (Fig.S2) with an accelerating voltage of 200 kV and scanning electron microscopy (SEM, Hitachi S-4800, with an acceleration voltage of 5 kV) (Fig. S3).

5.3 S_{BET} and pore size distribution. The surface area was obtained on a TriStar II 3020 using the Brunauer–Emmett–Teller (BET) method and measurement at -196 °C in nitrogen, as shown in Fig. S4. Prior to the measurement, all the photocatalysts were degassed under evacuation at 150 °C for 10 h. The pore size distribution was obtained by desorption isotherms using the Barret–Joyner–Halender (BJH) method as shown in Table S3.

5.4 XPS. X-ray photoelectron spectroscopy (XPS) dates (Fig. S5 and Table S4–S5) were obtained on a USA Thermo ESCALAB 250 with a monochromatized Al Ka line source (200 W). The binding energy correction was referenced to C 1s peaks (284.6 eV) arising from surface hydrocarbons. The spectra deconvolution was carried out by XPS PEAK41 software packages.

5.5 *In-situ* FT-IR. The setup (Fig. S7) consists of a (i) Bruker Tensor II FT-IR spectrometer equipped with a MCT detector and a (ii) Praying Mantis™ HVC accessory enclosed with a three-window dome; an (iii) ‘HARRICK ATC-024-4 temperature controller’; and a (iv) cooling water circulating system; (v) Xenon lamp. The ATC was controlled by a EZ-ZONE software. When testing highly purity Ar (25 mL min⁻¹) was used as carrier gas.

The tests were carried out according to the following procedures: (1) The fresh powder sample was loaded in the *in-situ* reaction cell. (2) After assembling the HVC with a sample into the spectrometer, the system was warmed to 120 °C with the introduction of Ar gas (25 mL min⁻¹) for 3 hour. The temperature was controlled by the ATC and cooling water. (3) After the thermal treatment, and until the HVC was cooled to 30 °C, 20 μL of the reaction liquid mixture (or water or methanol) was introduced to the HVC by dripping. (5) The cell was purged by the Ar gas (25 mL min⁻¹) to clean up the redundant substrates, meanwhile, IR spectra were collected repeatedly every 1 minute. The cell was continuously swept until the IR signals stable.

5.6 PL and TPL. Steady-state photoluminescence (PL) spectra were performed on a Hitachi F-7000 FL spectrophotometer at room temperature with an excitation wavelength of 365 nm (Fig. S8b). Time-resolved PL (TPL) decay curves were recorded on a FLS920 fluorescence lifetime spectrophotometer (Edinburgh Instruments, UK) under the excitation of 365 nm and probed at 460 nm. The decay curves can be well fitted by the following biexponential equations. $I_{(t)} = I_0 + A_1 \exp(-t/\tau_1)$; $\tau_a = A_1 \tau_1$

5.7 DRS. The UV–Vis diffuse reflectance spectra (DRS) were observed on a Shimadzu UV–3600 UV–Vis–NIR spectrophotometer using BaSO₄ as a reference and the diffuse reflectance accessory (Fig. S12).

5.8 FT–IR. Fourier transformed infrared (FT–IR) spectra were obtained on a Nicolet Magna–IR 550–II spectrometer using KBr as a standard reference sample, and the mass ratio between KBr and the sample was 50:1.

6. Photoelectrochemical Measurements.

Electrochemical tests [transient photocurrent (TP), Mott–Schottky plots and electrochemical impedance spectroscopy (EIS)] (Fig. S8-S9) were characterized on a workstation (CHI 760D, CH Instruments, Inc., Shanghai, China) in a three-electrode model. A Ag/AgCl electrode (saturated KCl) was used as a reference electrode and Pt wire was used as the counter electrode. Before measurement, the working electrode was prepared as follows: 5 mg of the catalyst powder was mixed with 0.5 g of 2 wt.% polyvinylidene difluoride (PVDF) N-methyl pyrrolidone (NMP) solution, and then, ultrasonication was performed until a homogeneous mixture was obtained. Finally, 20 μL of the slurry was spread onto the fluorine-doped tin oxide (FTO) glass electrode.

6.1 TP. The TP measurements were obtained using the Amperometric it Curve technique and performed under LED light illumination conditions. The working electrodes were immersed in 0.2 M Na₂SO₄ aqueous solution with the pH maintained at 6.6.

6.2 Mott–Schottky. Mott–Schottky plots were obtained using the impedance–potential technique with the working electrodes immersed in 0.2 M Na₂SO₄ aqueous solution with the pH maintained at 6.6. The potential conversion relation is according to the Nernst equation:

$$E(\text{NHE}) = E(\text{Ag/AgCl}) + 0.197 \quad (1)$$

$$E(\text{RHE}) = E(\text{NHE}) + 0.0591 \times \text{pH} \quad (2)$$

6.3 EIS. The electrochemical impedance spectra were also obtained on the abovementioned three–electrode system, by using the A. C. Impedance technique. The working electrodes were immersed in mixture aqueous solution. The composition of the mixed solution is as follows: 0.1 mol L⁻¹ KCl, 2 mmol L⁻¹ K₃[Fe(CN)₆] and 2 mmol L⁻¹ K₄Fe(CN)₆ 3H₂O.

7. Acidimetric titration of carbon nitride.

The acidic functional groups and the presences of such groups were determined by a neutralization adsorption experiment. Typically, 100 mg CNS and CNS-H samples were dispersed into 50 g of 0.05 mol L⁻¹ NaHCO₃ aqueous solution, respectively. The resultant mixtures were allowed to equilibrate with magnetic stirring for 6 h. After that, the mixtures were filtered and the filtrate was collected and 20 g of the mixture was pipetted out and back titrated using 0.025 mol L⁻¹ hydrochloric acid solutions. The concentrations of the NaHCO₃ aqueous solution was calibrated by standard hydrochloric acid. In the controlled reaction water was used to disperse the sample. After stirring for 6 h, 10 g filtrate was mixed with 25 g NaOH aqueous solution (FC mixture) and back titrated using 0.025 mol L⁻¹ hydrochloric acid solutions to determination of the acidity and alkalinity of the catalyst surface. Bromocresol green–methyl red was used as the indicator. The adsorbed base was calculated using the following equation:

$$n_A = \left(V_{A0} * \frac{C}{m_{A0}} - V_{A1} * \frac{C}{m_{A1}} \right) * \frac{m_A}{m_1} + n_F \quad (3)$$

$$n_F = \left[\left(V_F * C - V_{C0} * \frac{C * m_{FC}}{m_{C0}} \right) / m_{F1} \right] * m_F / m_2 \quad (4)$$

In the equations:

- C : Concentration of standard hydrochloric acid (mol·L⁻¹);
- V_{A0}: The hydrochloric acid volume used in calibrating base solution (mL);
- m_{A0}: The quality of base solution used in calibrating by hydrochloric acid (g);
- V_{A1}: The hydrochloric acid volume used in calibrating the above filtrate (mL);
- m_{A1}: The quality of base filtrate solution used in titration (g);
- m_A: The quality of base solution used in sample dispersion (g);
- m₁, m₂: The consumption quality of our sample (g).
- V_F: The hydrochloric acid volume used in calibrating FC mixture (mL);
- m_{FC}: The quality of FC mixture used in titration (g);
- m_{F1}: 10 g;
- m_F: The quality of water used in sample dispersion (g).

Table S1 H₂ evolution for CN and CNS_x under visible light irradiation ($\lambda > 420$ nm).

Entry	Sample	H ₂ /μmol (4 h)	Activity (μmol h ⁻¹ g ⁻¹)
1	CN	2.1	10.5
2	CNS _{0.25}	25.3	126.3
3	CNS _{0.50}	68.8	344.0
4	CNS _{0.75}	82.9	414.5
5	CNS	107.8	539.0

Reaction conditions : H₂O (64 mL), methanol (36 mL), catalyst (50 mg), N₂ (1 atm), Xenon lamp (300 mW cm⁻², > 420 nm), H₂PtCl₆ (0.1 M, 260 μL), 25 °C, 4 h.

Table S2 The content variation of cyano and carboxyl groups on the CNS-H_y samples.

Entry	Sample	Cyano group area	Conv. _{area} (%)	Carboxyl (mmol g ⁻¹)	Cyano group Estimated value (mmol g ⁻¹)
1	CNS	13.283	0.0	–	0.50
2	CNS-H _{1/6}	7.964	40.0	0.21	0.53
3	CNS-H _{0.5}	6.306	52.5	0.25	0.48
4	CNS-H ₁	5.067	61.9	0.30	0.48
5	CNS-H	3.021	77.3	0.40	0.52
6	CNS-H ₄	3.051	77.0	0.35	–

The cyano area was calculated by using the OMNIC software. As shown in Table S2, entry 2, the cyano area is decreased from 13.283 to 7.946. That indicates about 40.0% of the cyano had been hydrolyzed to carboxylic acid. The titration results of carboxyl group in CNS-H_{1/6} is 0.21 mmol g⁻¹, thus the total cyano content in CNS-H_{1/6} is about 0.53 mmol g⁻¹ (0.21 / 0.4 = 0.53). The treatment and cyano group conversion methods of other samples in entries 3-6 were same to CNS-H_{1/6}. The detailed cyano group content was 0.50 mmol g⁻¹ which taken the average of 0.53, 0.48, 0.46 and 0.52 mmol g⁻¹ in Table S2.

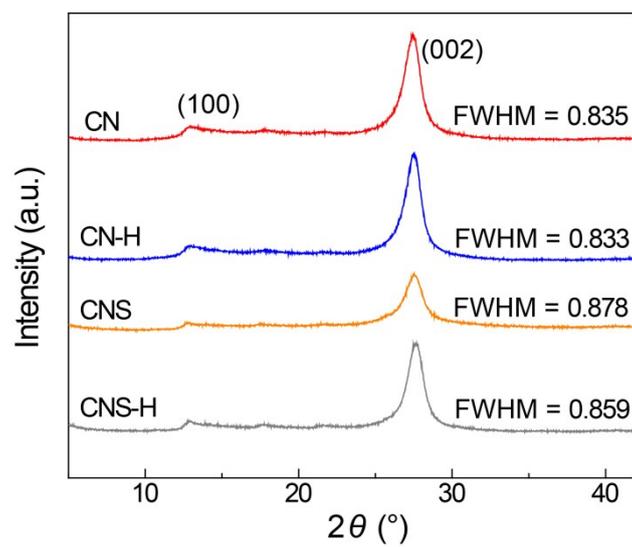


Fig. S1 XRD patterns of sample CN, CN-H, CNS and CNS-H.

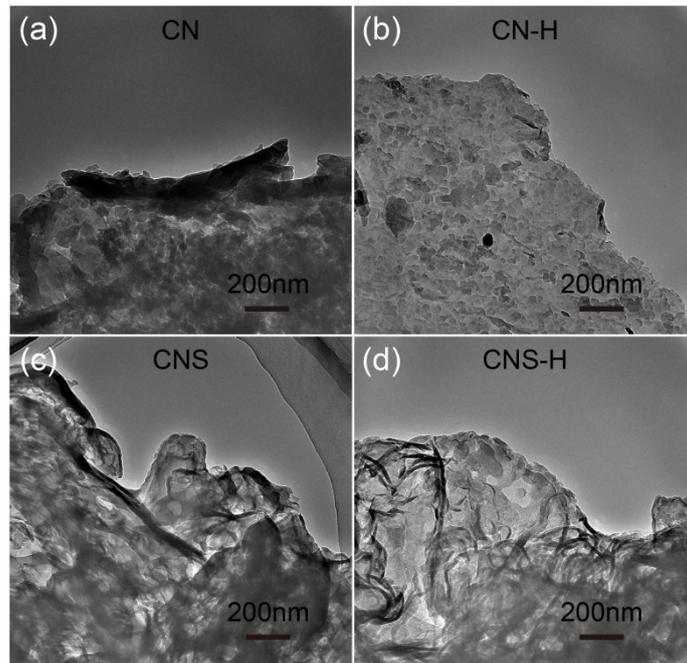


Fig. S2 TEM images of the CN, CN-H, CNS and CNS-H samples.

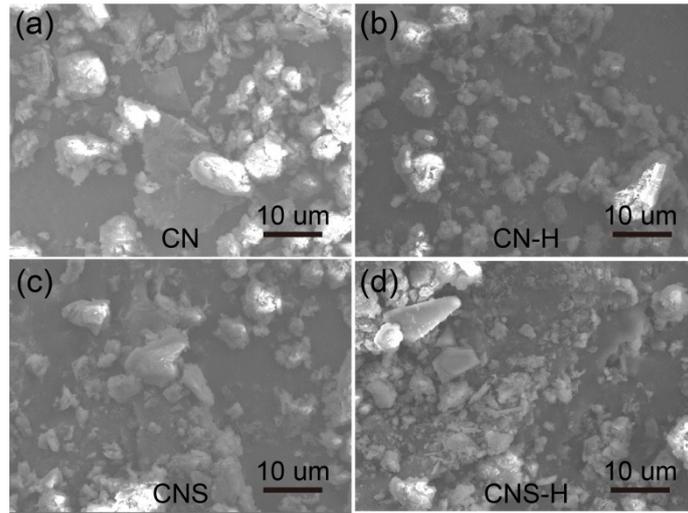


Fig. S3 SEM images of the CN, CN-H, CNS and CNS-H samples.

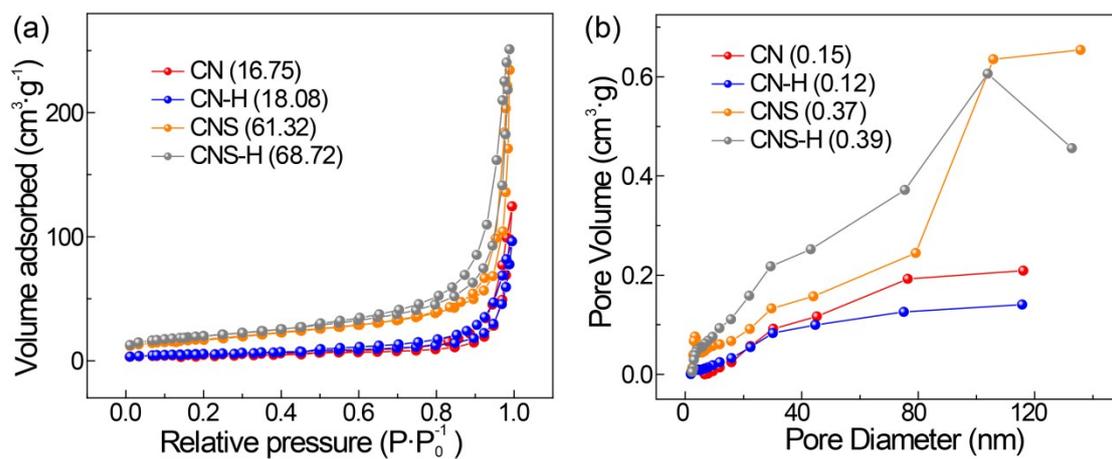


Fig. S4 (a) N₂ sorption isotherms and (b) the corresponding pore size distribution curves.

Table S3 Physicochemical properties of CN, CN-H, CNS and CNS-H.

Entry	Sample	S _{BET} (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)
1	CN	16.75	0.15
2	CN-H	18.08	0.12
3	CNS	61.32	0.37
4	CNS-H	68.72	0.39

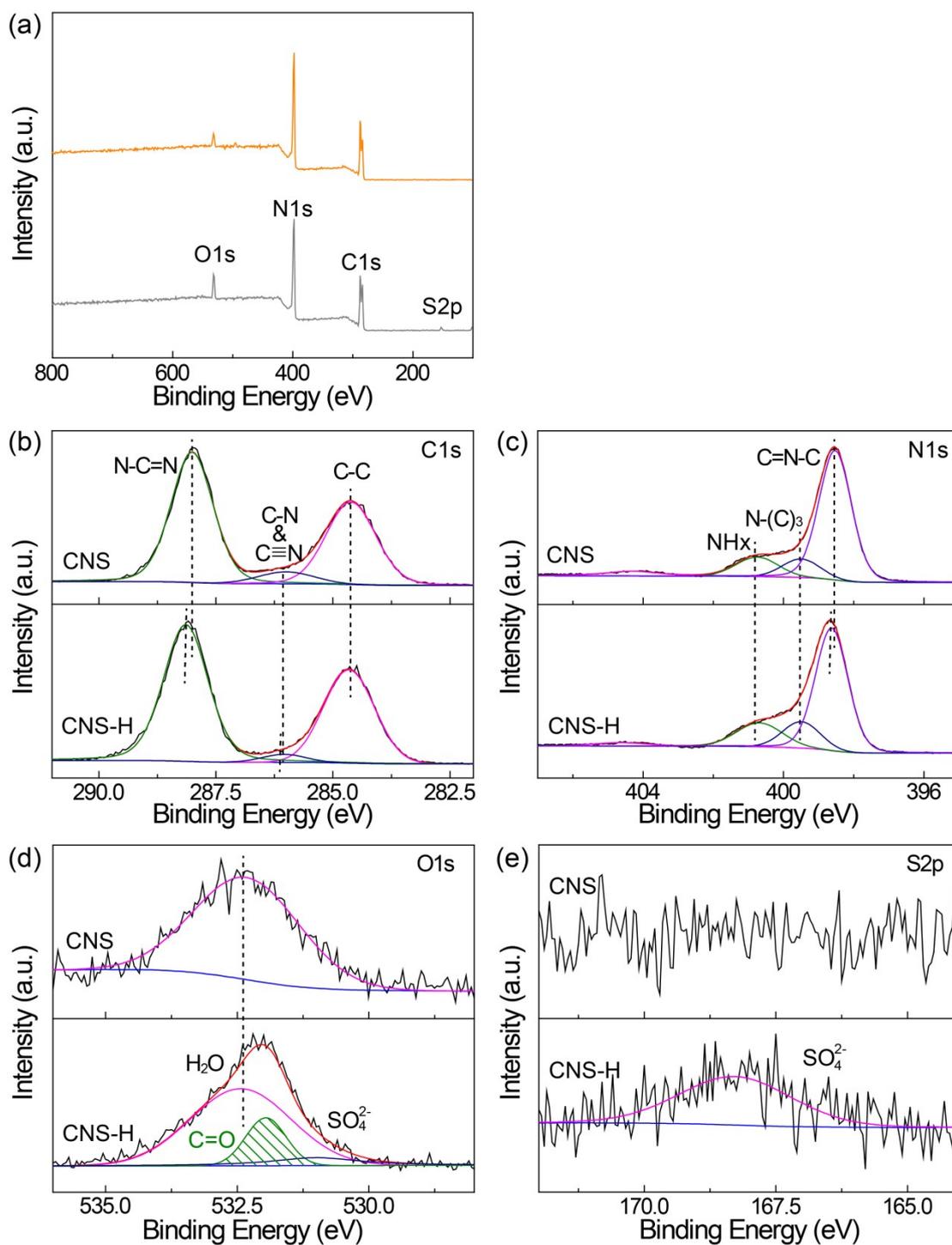


Fig. S5 The XPS (a) full (b) C1s (c) N1s (d) O1s and (e) S2p spectra of sample CNS and CNS-H.

Table S4 Distribution of element species obtained from the deconvolution of the C1s, N1s and O1s Peaks by XPS.

Sample	Element	Area	Atomic (%)	wt%
CNS	C	28965.96	52.91	48.6
	N	37579.3	42.21	45.4
	S	-	-	-
	O	7201.09	4.88	6.0
CNS-H	C	26713.26	51.63	47.0
	N	34910.76	41.73	44.3
	S	172.46	0.17	0.4
	O	9528.1	6.83	8.3
CN	C	27517.35	58.18	53.7
	N	26304.07	34.09	36.7
	O	9851.82	7.73	9.6

Table S5 Distribution of element species obtained from the deconvolution of the S2p and O1s Peaks by XPS.

Sample	Element	Area	wt%
CNS	S	-	-
	O (H ₂ O)	7201.09	6.0
CNS-H	S (SO ₄ ²⁻)	172.46	0.4
	O (H ₂ O)	6887.78	6.0
	O (C=O)	1721.95	1.5
	O (SO ₄ ²⁻)	918.37	0.8

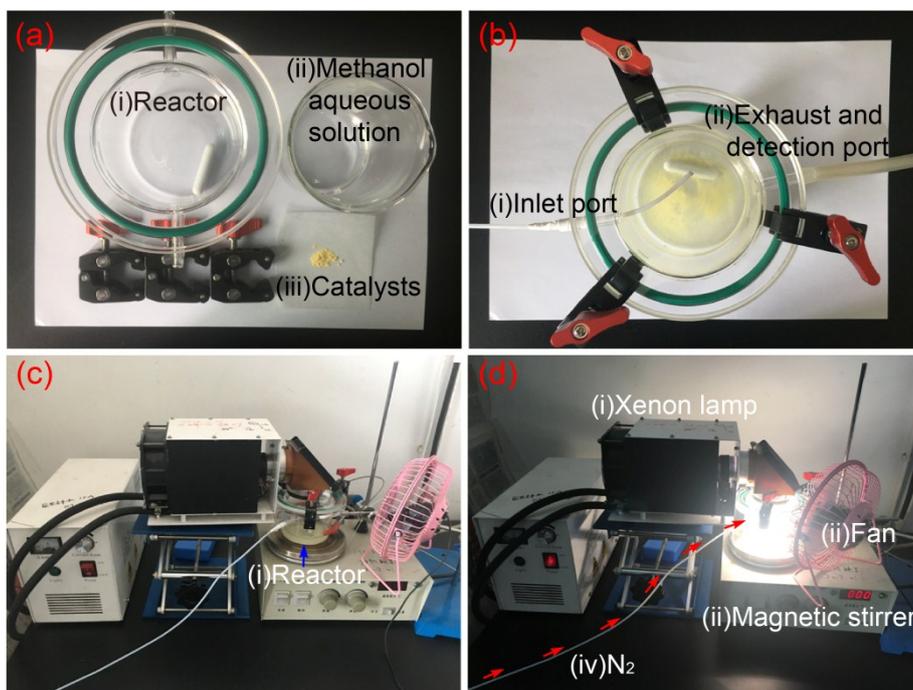


Fig. S6 Images of the experimental setups for (a), (b) reactor and (c), (d) photocatalytic oxidation reactions.

Table S6 H₂ evolution for CNS–H_y under visible light irradiation ($\lambda > 420$ nm).

Entry	Sample	H ₂ /μmol (4 h)	Activity (μmol h ⁻¹ g ⁻¹)
1	CNS	107.8	539.0
2	CNS–H _{1/6}	261.0	1305.0
3	CNS–H _{0.5}	295.1	1475.5
4	CNS–H ₁	328.7	1643.5
5	CNS–H	431.2	2156.0
6	CNS–H ₄	266.8	1334.0

Reaction conditions : H₂O (64 mL), methanol (36 mL), catalyst (50 mg), N₂ (1 atm), Xenon lamp (300 mW cm⁻², > 420 nm), H₂PtCl₆ (0.1 M, 260 μL), 25 °C, 4 h.

Table S7 H₂ evolution as the function of mole ratio between methanol and H₂O for CNS-H under visible light irradiation ($\lambda > 420$ nm).^a

Entry	Mole ratio (Methanol/H ₂ O)	H ₂ /μmol (4 h)
1	1/0 (Water free)	–
2	2/1	309.5
3	1/1	337.2
4	1/2	389.4
5	1/4	431.2
6	1/8	301.3
7	0/1 (Methanol free)	–

^a**Reaction conditions:** The total volume of solution is 100 mL, catalyst (50 mg), N₂ (1 atm), Xenon lamp (300 mW cm⁻², > 420 nm), H₂PtCl₆ (0.1 M, 260 μL), 25 °C, 4 h. A dash (–) means not detected.

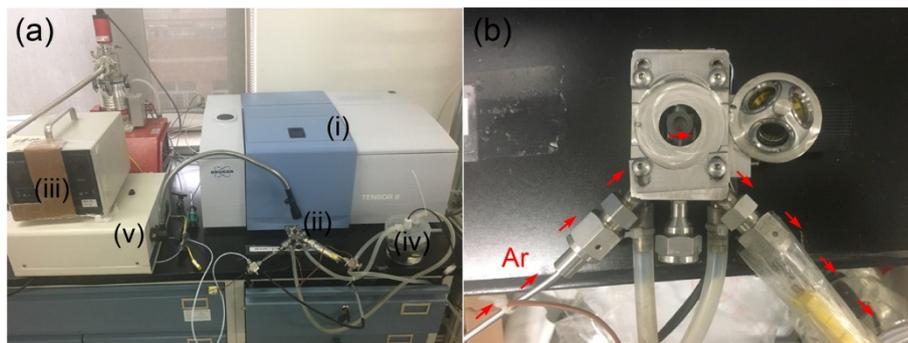


Fig. S7 Photographs of (a) *in-situ* FT-IR setup, (b) HVC accessory.

In **Fig. S7a**, the digital coding represents (i) Bruker Tensor II FTIR spectrometer, (ii) HVC accessory, (iii) HARRICK ATC-024-4 temperature controller, (iv) cooling water circulating system and (v) Xenon lamp.

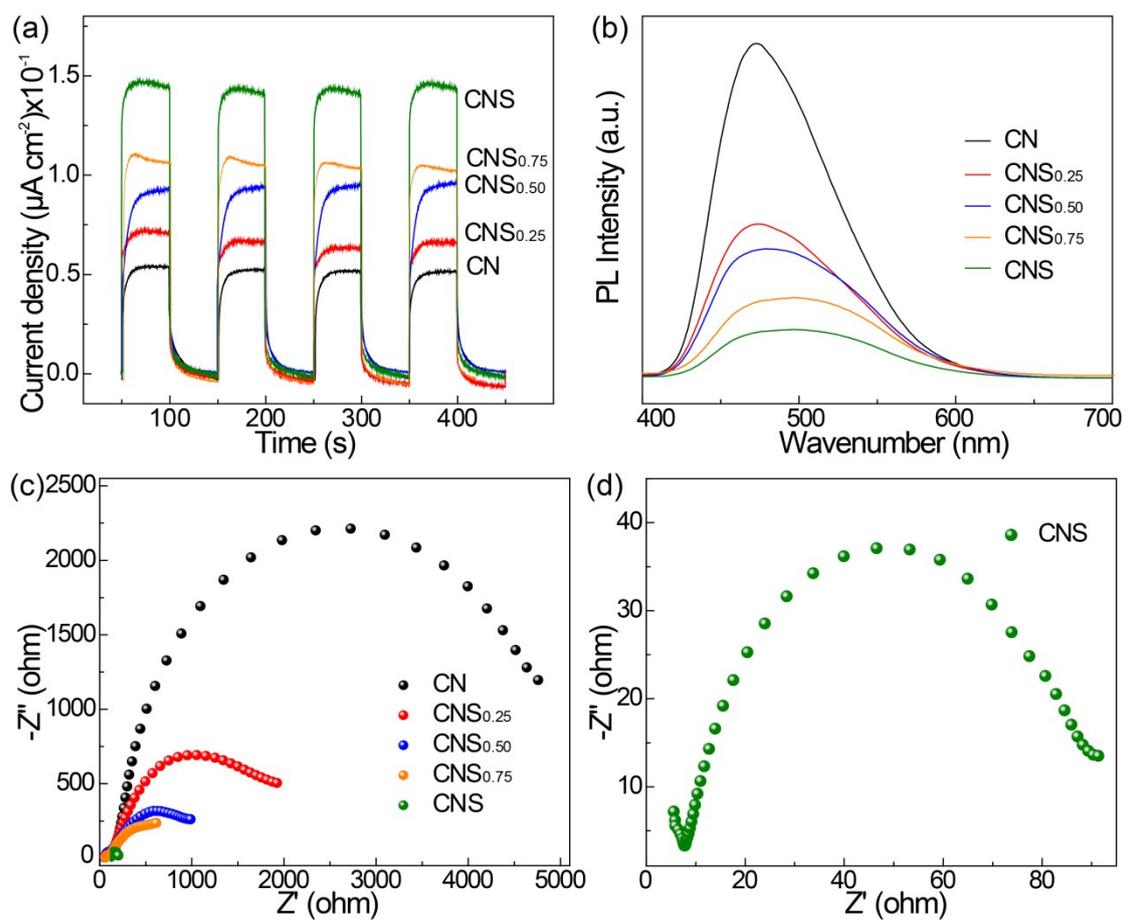


Fig. S8 The photoelectric properties. (a) photoelectrochemical responses (b) photoluminescence ($\lambda_{\text{excitation}} = 365 \text{ nm}$, room temperature) and (c) EIS spectra of CN, CNS_{0.25}, CNS_{0.50}, CNS_{0.75} and CNS. (d) The enlarged EIS spectra of CNS.

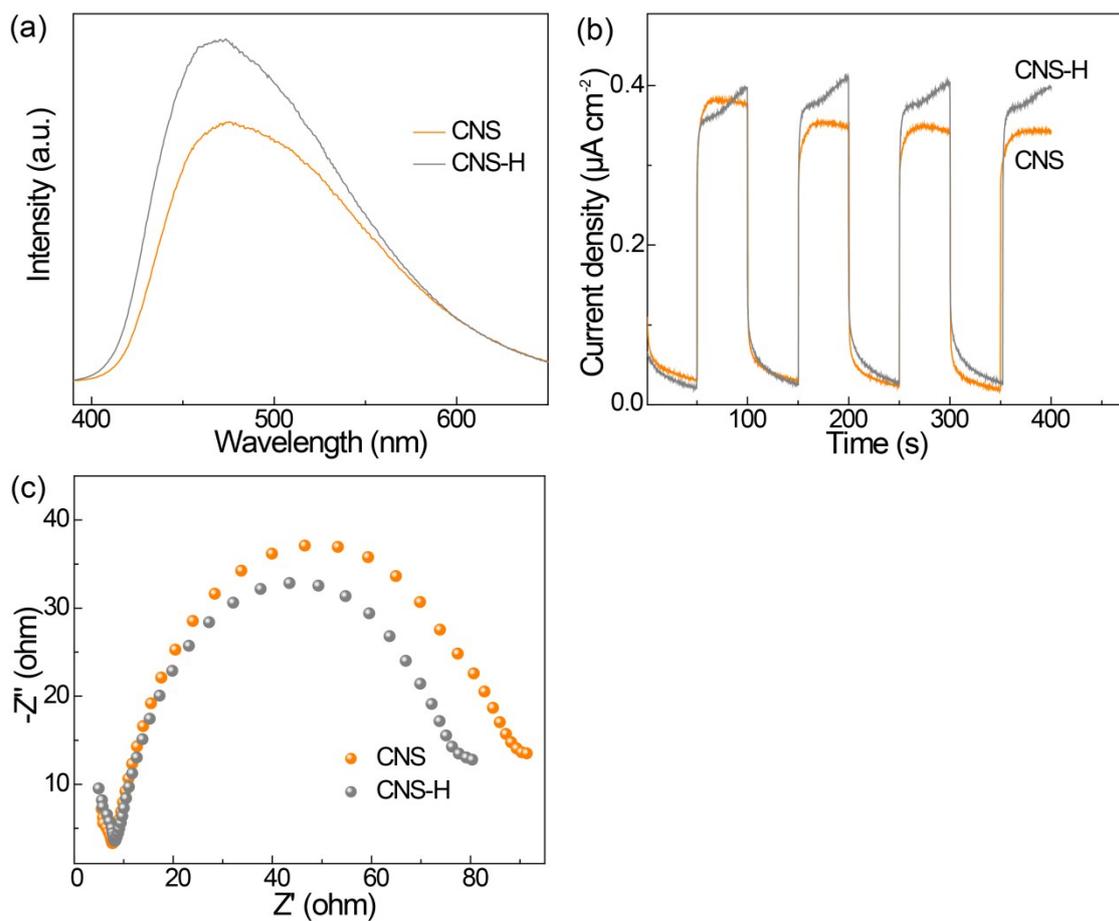


Fig. S9 The (a) photoluminescence ($\lambda_{\text{excitation}} = 365 \text{ nm}$, room temperature) (b) photoelectrochemical responses and (c) EIS spectra of CNS and CNS-H.

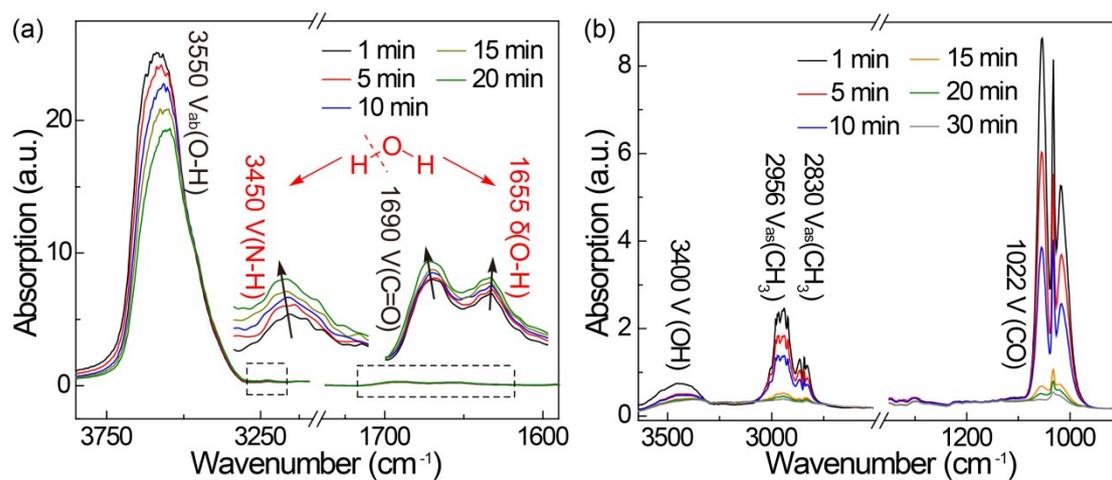


Fig. S10 FT-IR spectra detail purge time induced growth and decay of (a) H₂O and (b) methanol bands on CNS-H in the dark. The FT-IR were obtained in a sealed *in situ* reaction cell, the dosage of the H₂O and methanol is 20 μL, respectively.

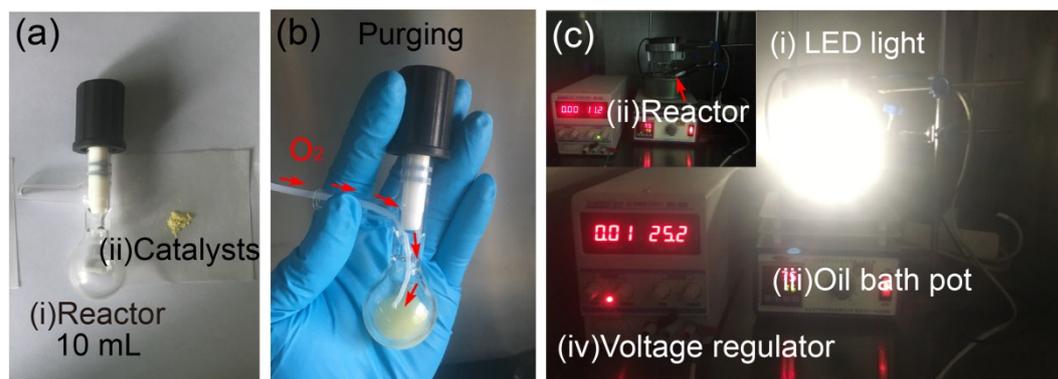


Fig. S11 Images of the experimental setups for (a) reactor (b) O₂ purging and (c) photocatalytic oxidation reactions.

Table S8 Photocatalytic activity for benzyl alcohol oxidation over varied carbon nitride catalysts under visible light.

Entry	Sample	Yield (%)
1	CN	26.7
2	CNS	35.9
3	CNS-H	99.9

Reaction condition: Benzyl alcohol oxidation (0.2 mmol), acetonitrile (2 mL), catalyst (10 mg), O₂ (1 atm), white LED light (400 mW cm⁻²), 60 °C, 10 h.

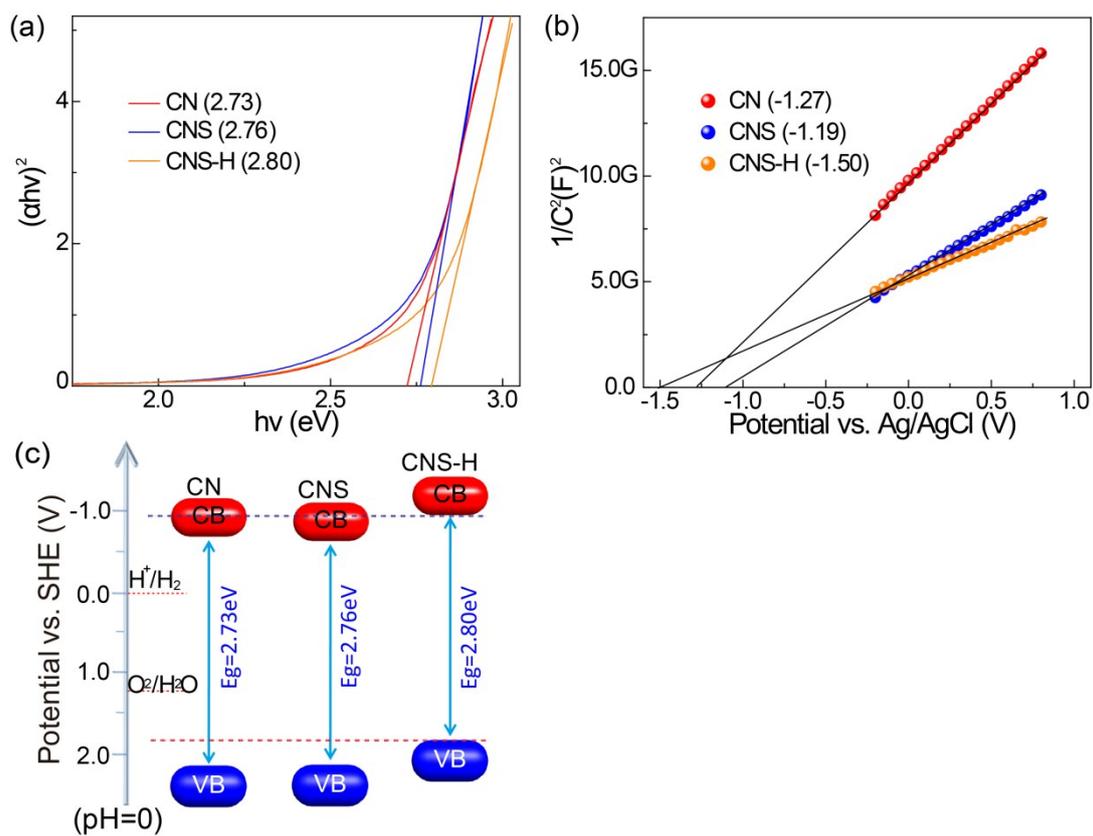


Fig. S12 (a) Band gap energy (b) Mott–Schottky plots and (c) band gap structure of CN, CNS and CNS-H.

As presented in **Fig. S12b**, the flat band potentials of CN, CNS and CNS-H are determined to be at -1.27 V, -1.19 V and -1.50 V vs. Ag/AgCl at pH = 6.8, which correspond to -0.68 V, -0.60V and -0.91 V vs. SHE at pH = 0, respectively (according to eq.1 and eq.2).

Table S9 Time course of H₂ and CO₂ evolution for CNS–H under visible light irradiation ($\lambda > 420$ nm).

Entry	Time (h)	H ₂ (μmol)	CO ₂ (μmol)	Mole ratio (H ₂ /CO ₂)
1	1	26.0	8.5	3.05
2	2	105.7	33.4	3.16
3	3	240.7	76.7	3.14
4	4	431.2	134.8	3.20

Reaction conditions : H₂O (64 mL), methanol (36 mL), catalyst (50 mg), N₂ (1 atm), Xenon lamp (300 mW cm⁻², > 420 nm), H₂PtCl₆ (0.1 M, 260 μL), 25 °C.

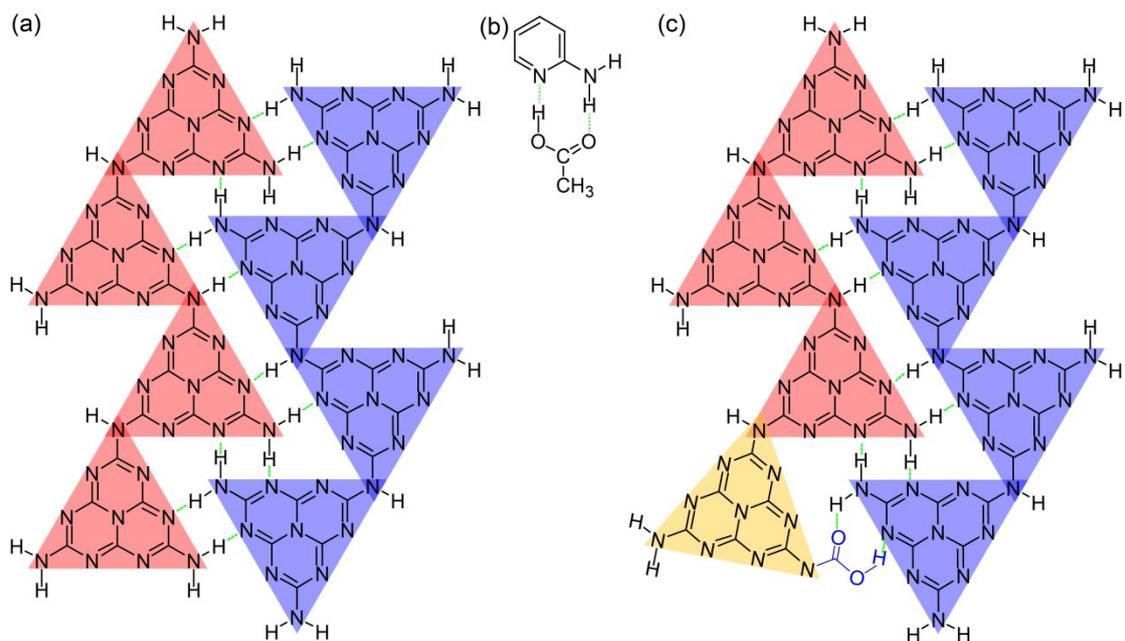


Fig. S13 Atomic structures of carbon nitride and nitrogen-containing heterocyclic/acid compounds with hydrogen bonds. (a) the atomic structure of carbon nitride. Two nearest neighboring melon strands within the basal plane of monolayer carbon nitride are masked by solid red and blue triangles. (b) the atomic structure of 2-aminopyridine/acid system referred the Ref 3³ in this SI. (c) the atomic structure of carboxylic acid modification carbon nitride. The carboxylic acid modification melon is masked by solid yellow triangle.

References

- 1 B. Yuan, Z. Chu, G. Li, Z. Jiang, T. Hu, Q. Wang, C. Wang, *J. Mater. Chem. C* 2014, **2**, 8212.
- 2 V. W. H. Lau, I. Moudrakovski, T. Botari, S. Weinberger, M. B. Mesch, V. Duppel, J. Senker, V. Blum, B. V. Lotsch, *Nat. Commun.* 2016, **7**, 12165.
- 3 S. Chai, G.-J. Zhao, P. Song, S.-Q. Yang, J.-Y. Liu, K.-L. Han, *Phys. Chem. Chem. Phys.* 2009, **11**, 4385.