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Supporting Information

Two-dimensional Graphitic Carbon Nitride/N-doped Carbon with Direct Z-scheme Heterojunction for Photocatalytic Generation of Hydrogen

Jing Wang, [a‡] Youcai Sun, [a‡] Jianwei Lai, [b] Runhui Pan, [a] Yulei Fan, [a] Xiongwei Wu, [c] Man Ou, [a] Yusong Zhu, [a] Lijun Fu, [a] Feifei Shi, [*b] and Yuping Wu[*a]

[a.] *College of Chemical Engineering and School of Energy Science and Engineering, Nanjing Tech University. Nanjing, Jiangsu, 211816, China. Email: wuyp@njtech.edu.cn*

[b.] *John and Willie Leone Family Department of Energy and Mineral Engineering, Pennsylvania State University, University Park, PA, 16802, USA. Email: feifeishi@psu.edu (Shi)*

[c.] *School of Chemistry and Materials Science, Hunan Agricultural University, Changsha, 410128, China.*

‡These authors contributed equally.

Experimental sections

Preparation of N-doped carbon (NC)

NC was prepared by a simple hydrothermal method. Typically, 0.48 g of citric acid and 0.45 g of urea were dissolved in 10 ml deionized water. The above aqueous solution was transferred into a Teflon-sealed autoclave and heated for 8 h at 180 °C. After cooling it to room temperature, the product was collected by centrifuging.

Synthesis of bulk g-C_3N_4 (bulk C_3N_4)

Firstly, 5.0 g melamine was put into an alumina crucible with a cover and heated to 520 °C for 4 h with a ramping rate of 5 °C/min. After cooling it down naturally, the resultant agglomerate was ground into yellow powders, denoted as bulk C_3N_4.

Synthesis of C_3N_4

Typically, 1.0 g of bulk C_3N_4 and 5.0 g of NH_4Cl mixed thoroughly in a ball mill. Then, the mixture was treated at 550 °C for 3 h at a heating rate of 3 °C/min. The as-synthesized samples were denoted as C_3N_4.

Synthesis of 2D C_3N_4/NC

2D C_3N_4/NC were prepared via a polymerization method. Specifically, C_3N_4 was modified with NC via a gas-blowing method. This is a process of calcining the mixture of NC, bulk C_3N_4, and NH_4Cl. Typically, 1.0 g of bulk C_3N_4, a certain amount of NC, and 5.0 g of NH_4Cl mixed thoroughly in a ball mill. Then, the mixture was treated at 550 °C for 3 h with a heating rate of 3 °C/min. The as-synthesized samples were denoted as C_3N_4/NC-I, C_3N_4/NC-II, C_3N_4/NC-III, where I, II, and III represent that the mass ratios of NC in C_3N_4/NC photocatalyst are 0.05, 0.075, 0.10 wt %, respectively.

Characterization

XRD patterns were collected by a BRUKER AXS GMBH (D8 ADVANCE) machine with Cu Kα radiation at the angle range of 10-90^{o} (2θ). TEM images were recorded on a JEOL JEM-2100 transmission electron microscope (acceleration voltage of 200 kV). The UV-visible diffuse reflectance spectra were measured on an ultraviolet-visible spectrophotometer (UV 2600, Shimadzu Co.). Nitrogen adsorption and desorption measurements were carried out on an Autosorb iQ instrument, the surface areas were calculated by the Brunauer-Emmett-Teller (BET) method. Raman spectra were recorded on a Raman microscope (LABRAM-HR, JY Co.). XPS measurements were performed on a Kratos AXIS Ultra DLD spectrometer with a monochromatic Alka X-ray source. Thermogravimetric differential scanning calorimetry (TG-DSC) was performed on a NETZSCH STA449F3 (Germany) instrument. Fourier transform infrared spectra (FTIR) were recorded on Thermo Scientific spectrometer (Nicolet iS-5) in the frequency range of 4000 cm^{-1}-450 cm^{-1}. Photoluminescence (PL) spectra were collected on an Edinburgh spectrofluorometer (FLS980).

Electrochemical measurements

The transient photocurrents (I-t), and electrochemical impedance spectroscopy (EIS) measurements of as-prepared samples were conducted on a CHI660E electrochemical workstation with a three-electrode system, where a sample-coated fluoride-tin oxide (FTO) glass was used as the working electrode, a saturated calomel electrode (SCE) and a Pt wire were acted as the reference electrode and counter electrode, respectively. The solution of 0.2 M Na_2SO_4 purged with nitrogen was the electrolyte. A 300 W Xenon lamp with a 400 nm cutoff filter was chosen to be a light source. The working electrode was fabricated as following procedures: 5 mg of the photocatalyst was dispersed in 1 ml ethanol solution containing 20 μl Nafion solution (5%) with constant sonication for 30 min, and then it was spin-coated on the FTO substrate (10 mm × 1.5 mm) and dried at 150 °C for 40 min.

Photocatalytic H_2 evolution measurements

The photocatalytic experiment of H_2 evolution was carried in an online evacuation system (Perfectlight Labsolar-6A system), A 300 W Xe lamp (CEL-HX300) with a 400 nm cutoff filter was used as light source. Briefly, 10 mg photocatalysts dispersed in an 80 mL aqueous solution containing 10 vol % triethanolamine (TEOA) as the electron donor. 1 % Pt nanoparticles were deposited on the surface of as-synthesized catalysts via an in-situ photochemical method using K_2PtCl_6 as a precursor. Before irradiation, the suspension was degassed for 30 min to thoroughly remove the dissolved air in electrolyte. The experimental temperature was controlled at 6 °C by adopting a liquid trap system with water circulation. The evolved gases were quantitatively analyzed every one hour by the gas chromatography (FULI 979011) equipped with a TCD and 5 Å molecular sieve column.

The external quantum efficiency (EQE) calculation

EQE has been determined using the follow equation：

$$EQE = \frac{the\ number\ of\ reacted\ electrons}{the\ number\ of\ incident\ photons} \times 100\%$$

Where the number of reacted electrons can be used for the molecule of H_2 evolution, and the number of incident photons is the photons number reaching the surface of catalysts. The H_2 generation rate was measured in the same reaction system as predicted in the experimental section. In addition, photocatalysts were irradiated with monochromatic light generated by equipping with a bandpass filter (400 nm). The numbers of photons were obtained according to the follow equation:

$$N = \frac{E\lambda}{hc}$$

Where E, λ, h and c are the light intensity, wavelength, Planck constant and velocity of light, respectively.

The calculation process of C_3N_4/NC:

$$N = \frac{E\lambda}{hc} = \frac{40.5 \times 10^{-3} \times 3600 \times 400 \times 10^{-9}}{6.626 \times 10^{-34} \times 3 \times 10^{8}} = 2.93 \times 10^{20}$$

$$EQE = \frac{the\ number\ of\ reacted\ electrons}{the\ number\ of\ incident\ photons} \times 100\%$$

$$= \frac{2 \times the\ number\ of\ evolved\ H_2\ molecules}{N} \times 100\%$$

$$= \frac{2 \times 6.02 \times 10^{23} \times 8.637 \times 16.53 \times 10^{-6}}{2.93 \times 10^{20}} \times 100\% = 6.79\%$$

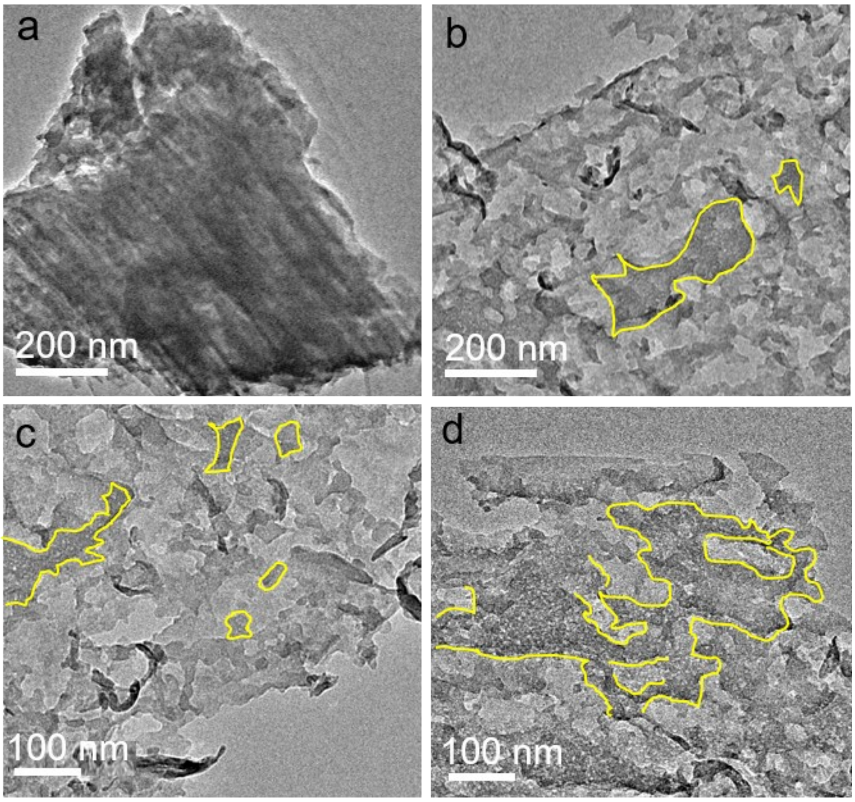

Fig. S1 TEM images of photocatalysts. (a) bulk C_3N_4; (b) C_3N_4/NC; (c) C_3N_4/NC-I; (d) C_3N_4/NC- III. C_3N_4/NC, C_3N_4/NC-I, and C_3N_4/NC-III were prepared with the NC mass ratio in C_3N_4/NC of 0.05%, 0.075%, and 0.10%, respectively. NC was marked with yellow line.

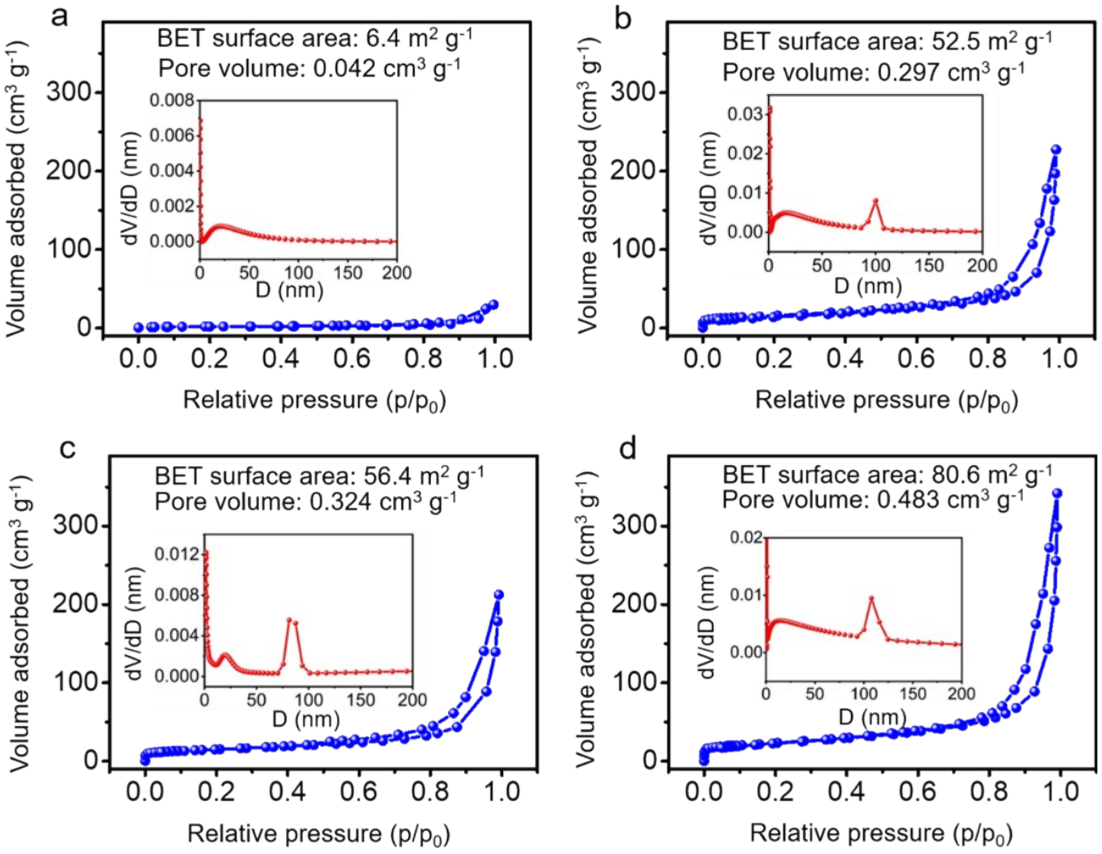

Fig. S2 N_2 adsorption-desorption isotherms and pore size distribution plots (inset). (a) bulk C_3N_4; (b) C_3N_4; (c) C_3N_4/NC-I; (d) C_3N_4/NC- III. C_3N_4/NC-I and C_3N_4/NC-III were prepared with the NC mass ratio in C_3N_4/NC of 0.05% and 0.10%, respectively.

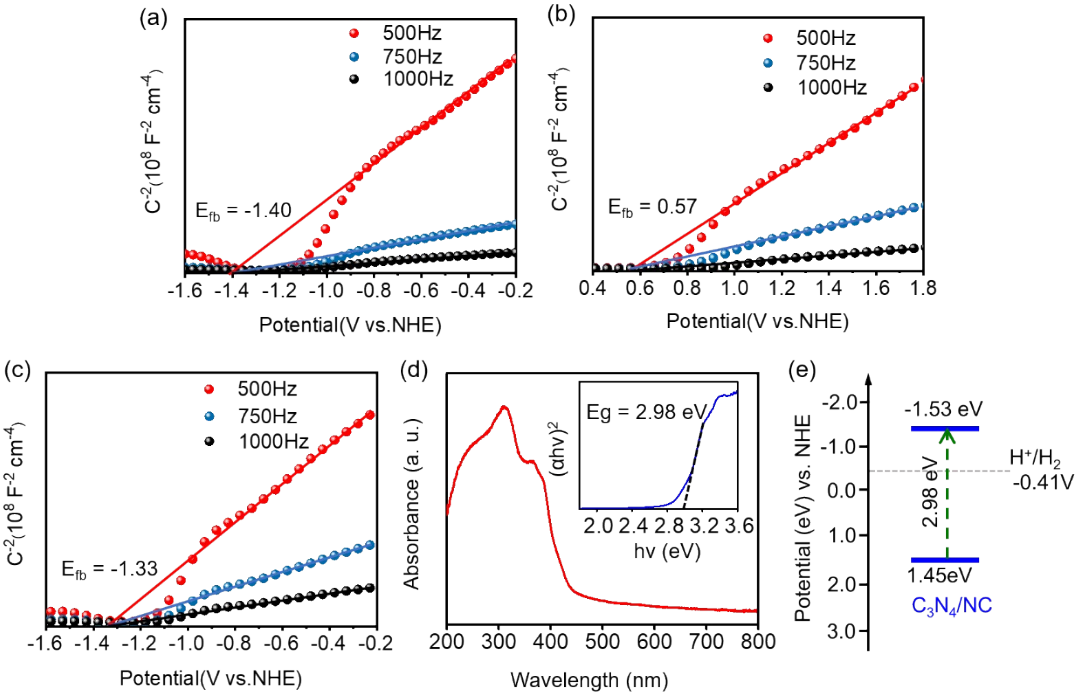

Fig. S3 (a-c) Mott-Schottky measurements of C_3N_4, NC, and C_3N_4/NC, respectively; (d) Light absorption and E_g spectra (the insert plot) of C_3N_4/NC; (e) Band structure of C_3N_4/NC.

In Fig S3 a-c, the E_{fb} of C_3N_4, NC, and C_3N_4/NC are -1.4, 0.57, and -1.33 V versus the normal hydrogen electrode (vs. NHE), respectively. Generally, the conduction band (CB) position is 0.2 eV higher than the flat-band potential (E_{fb}) for n-type semiconductor. So, the (CB) positions of C_3N_4, NC, and C_3N_4/NC are -1.6, 0.77, and -1.53 eV, respectively. Based on the bandgaps and CB positions (Fig. 4a, b, and Fig. S3a-d), VB positions of C_3N_4, NC, C_3N_4/NC are 1.42, 3.11, and 1.45 eV, respectively. These results not only are consistent with those in Fig. 4d, but also prove that the strong interaction between C_3N_4 and NC leads to the change of CB/VB levels.

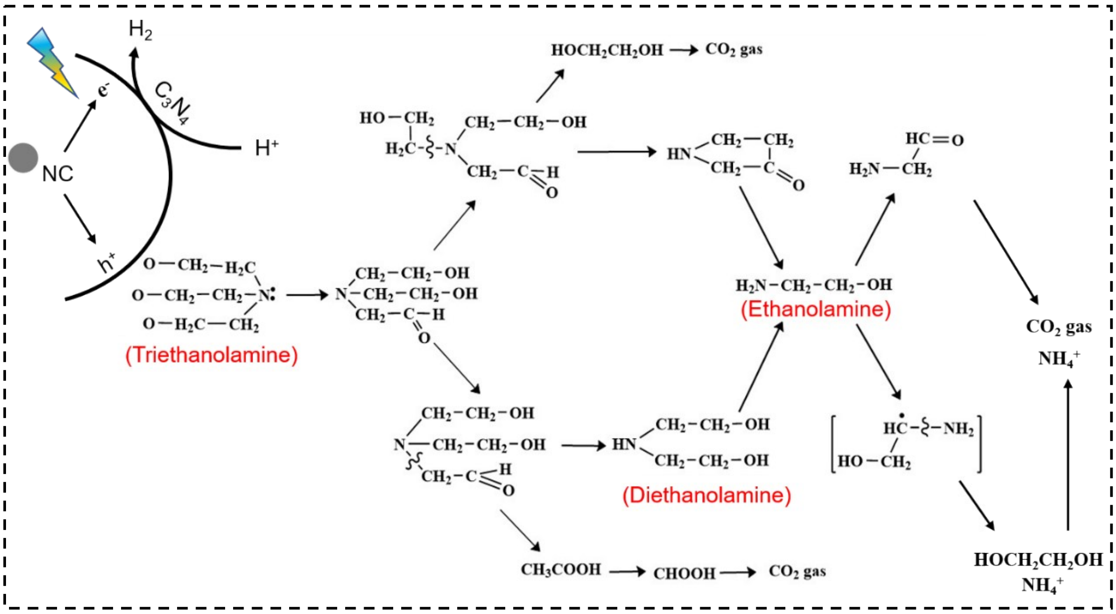

Fig. S4 The mechanism of holes oxidation TEOA reaction.

The reaction mechanism including the H_2O reduction and TEOA oxidation reaction was added. The oxidation reaction route is pretty complicated, undergoing decarbonization and denitrification reactions. [S1]

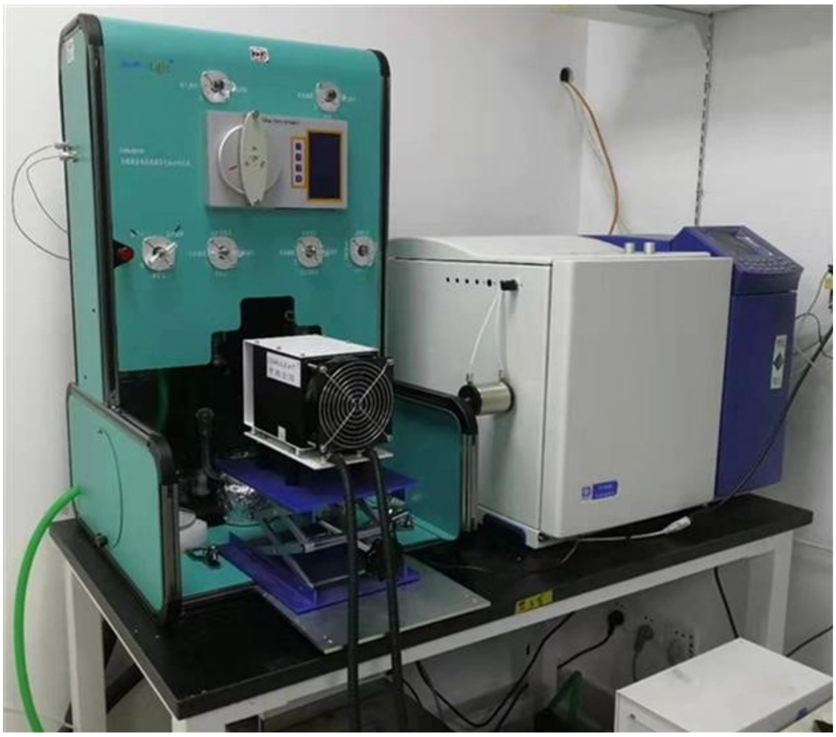

Fig. S5 Online photocatalytic test system.

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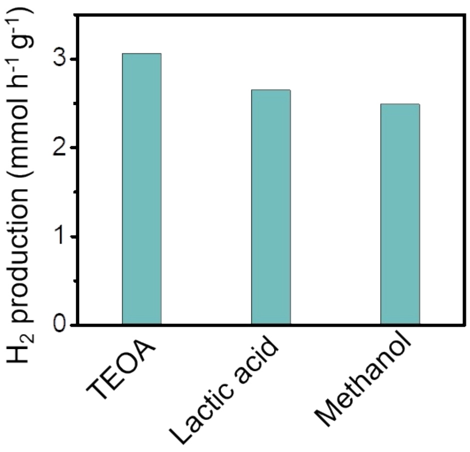


Fig. S6 The photocatalytic rate over C_3N_4/NC measured in different sacrificial reagents (TEOA, lactic acid, and methanol).

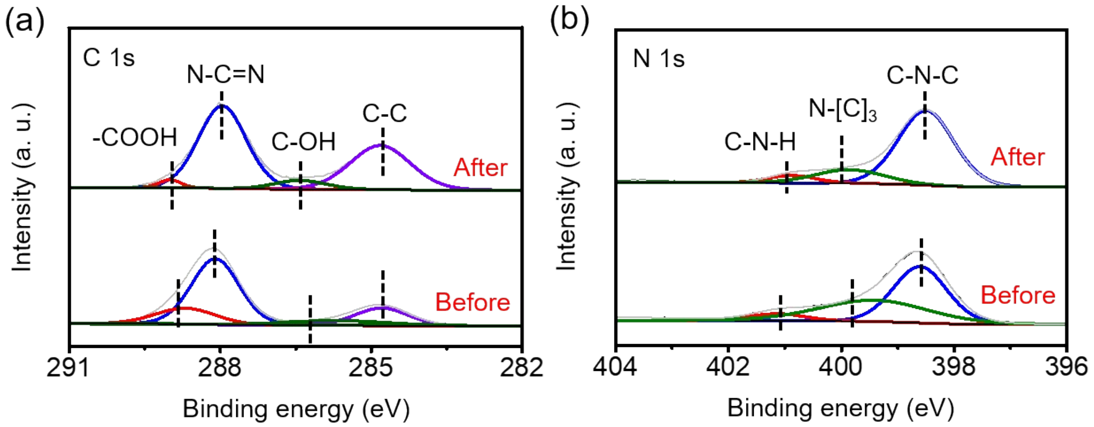
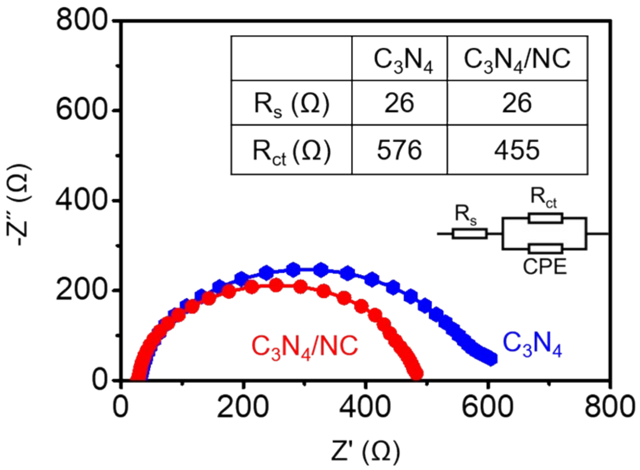


Fig. S7 XPS spectra of C_3N_4/NC before and after photocatalytic H_2 evolution reaction. (a) C 1s; (b) N 1s.



	C_3N_4	C_3N_4/NC
R_s (Ω)	26	26
R_{ct} (Ω)	576	455

Fig. S8 The EIS comparison of C_3N_4 and C_3N_4/NC. R_{ct} is the equivalent Randle circuit composed of the interfacial charge transfer resistance at the electrode/electrolyte interface; R_s is the electrolyte solution resistance; CPE is the constant phase element.

Table S1 Percentage of various atomic bonds obtained from XPS C 1s and N 1s spectra.

Sample	C-C	N-C=N	-COOH	C-N=C	N-(C)$_3$	C-N-H
C_3N_4	31.5	59.40	0	67.01	18.81	0
C_3N_4/NC	20.03	65.30	14.67	55.65	30.19	14.16

Table S2 Comparison of H_2 production for carbon modified C_3N_4.

Photocatalyst	**Co-catalyst**	$\frac{\textbf{Photocatalyst (mg)}}{\textbf{Reaction solvent (ml)}}$	**H_2 evolution rate**	**Ref**
g-C_3N_4/NC	0.5 wt% Pt	$\frac{10\,mg}{20\,ml}$	23 μmol h^{-1} g^{-1}	S2
ND@ g-C_3N_4	1.0 wt% Pt	$\frac{50\,mg}{100\,mg}$	59.1 μmol h^{-1}	S3
N-doped graphitic carbon-incorporated g-C_3N_4	3.0 wt% Pt	$\frac{50\,mg}{100\,ml}$	64 μmol h^{-1} g^{-1}	S4
UCN/CQDs	0.2 wt% Pt	$\frac{50\,mg}{100\,ml}$	88.1 μmol h^{-1}	S5
CNNS/CQDs	3.0 wt% Pt	$\frac{50\,mg}{100\,ml}$	116.1 μmol h^{-1}	S6
Amorphous carbon/g-C_3N_4	1.0 wt% Pt	$\frac{50\,mg}{80\,ml}$	212.8 μmol h^{-1} g^{-1}	S7
CNNS/CQDs	/	$\frac{10\,mg}{10\,ml}$	219.5 μmol h^{-1} g^{-1}	S8
CN/N-C/Pt	3.0 wt% Pt	$\frac{50\,mg}{50\text{ ml}}$	685 μmol h^{-1} g^{-1}	S9
C_3N_4/NC	1.0 wt% Pt	$\frac{10\text{ mg}}{80\text{ ml}}$	3060 μmol h^{-1} g^{-1}	**This work**

Table S3 Comparison of H_2 production for NiS or MoS_X modified C_3N_4.

Photocatalyst	**Co-catalyst**	$\frac{\textbf{Photocatalyst (mg)}}{\textbf{Reaction solvent (ml)}}$	**H_2 evolution rate (μmol h^{-1} g^{-1})**	**Ref**
NiS/g-C_3N_4	NiS	$\frac{50\,mg}{80\,ml}$	244	S10
MoS_2/g-C_3N_4	MoS_2	$\frac{50\,mg}{250\,ml}$	1155	S11
MoS_x/g-C_3N_4	MoS_x	$\frac{10\,mg}{100\,ml}$	1586	S12
g-C_3N_4/NiS	NiS	$\frac{50\,mg}{80\,ml}$	593.6	S13
NiS_2/g-C_3N_4	NiS_2	$\frac{50\,mg}{80\,ml}$	116.34	S14
g-C_3N_4/Ni/NiS	NiS	$\frac{50\,mg}{100\,ml}$	515	S15
C_3N_4/NC/Pt	Pt	$\frac{10\,mg}{80\,ml}$	3060	**This work**

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