

Supporting Information for:

Phosphorus- and Fluorine- Co-doped Carbon Nitride: Modulated Visible Light Absorption, Charge Carrier Kinetics and Boosted Photocatalytic Hydrogen Evolution

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1. Experimental section

1.1 Catalysts preparation

Phosphorus- or/and fluorine- carbon nitride photocatalysts were obtained by the traditional solid-state reaction, using sodium pyrophosphate as the phosphorus source and ammonium fluoride as fluorine source. Briefly, 5 g melamine mixed with amount of sodium pyrophosphate or/and ammonium fluoride was calcined at 550 °C for 4 h with the heating rate of 5 °C/min. And the cooling rate was also 5 °C/min. The obtained light yellow product was obtained after washing three times with deionized water and ethyl alcohol. The prepared P-doped, F-doped and P-, F-co-doped carbon nitride samples were named as P-CN, F-CN and PF-CN, respectively. The pristine g-C₃N₄ sample was obtained by the same experimental method as described above in the absence of sodium pyrophosphate and ammonium fluoride.

1.2 Sample characterization

The wide-angle X-ray power diffraction (XRD) performing on a Rigaku DMAX2500 X-ray diffractometer with Cu K α radiation was carried out in order to investigate the crystal phase structures. Transmission electron microscopy (TEM) was performed on a FEI Tecnai G2 F20 S-TWIN field emission microscope apparatus with an acceleration voltage of 200 kV, which applied to investigate the morphologies of the obtained photocatalysts. Perkin Elmer UV/VS/NIR Lambda 750 s spectrometer was performed to measure the ultraviolet-visible DRS of the obtained products. X-ray Photoelectron Spectroscopy (XPS) analyses were performed on an ESCALab220i-XL with a monochromatic Al K α and charge neutralizer. The C 1s peak at 284.6 eV was used for the referenced binding energy for samples. The specific surface areas of samples were measured by a Micromeritics ASAP 2020 Surface Area and Porosity Analyzer by Brunauer-Emmett-Teller (BET) technique. The photoluminescence (PL) and time-resolved fluorescence decay spectra were measured on an Edinburgh Instruments FLS920 spectrofluorimeter equipped with both continuous and pulsed xenon lamps. The wavelength of excitation light for emission spectra and transient decays was 310 nm for all samples. The transient photocurrent response of the samples with light on/off cycles were carried out on the Metrohm Autolab (PGST AT302N) under white (neutral) light irradiation (LED 690 lm, [Na₂SO₄] = 0.2 M) biased at 0.5 V vs. Ag/AgCl (saturated KCl). Electrochemical impedance spectroscopy (EIS) measurements were performed to investigate the migration rate of charge carrier with the frequency from 0.1 Hz to 100 KHz. Na₂SO₄ aqueous solution (0.2 M, pH = 7) was served as the electrolyte. Mott-Schottky plots of carbon nitrogen

were performed at the frequency of 500 Hz, 1000 Hz and 1500 Hz in the dark. Electron paramagnetic resonance (EPR) spectra for $\cdot\text{O}_2^-$ and $\cdot\text{OH}$ were determined in dark and under visible light irradiation (methanol solution volume, 2.0 mL; sample, 4 mg; DMPO, 0.22M).

1.3 Photocatalytic hydrogen evolution

Photocatalytic hydrogen production activity was conducted in a quartz flask sealed system with a side window for irradiation. The light source was a 300 W xenon lamp with a 420 nm cutoff filter ($\lambda \geq 420$ nm). In experiment, 100 mg sample was dispersed in a mixture of 80 mL deionized water and 20 mL triethanolamine (TEOA) which served as a sacrificial agent. The solution was evacuated to drive away air in the reaction before illumination. The yield of H_2 production was investigated on an online gas chromatograph (GC-7920, TCD, Ar as the carrier). The recycle test was carried out under the same experimental conditions for four runs. After the completion of the every round test, the catalyst was washed with water and recovered for next recycling.

The apparent quantum efficiency (AQE) was confirmed by using $\text{AQE} (\%) = (2 \times \text{Numbers of } \text{H}_2 / \text{Numbers of incident photons}) \times 100$. The light source used in experiment was a 300 W Xenon lamp with different wavelength filter. And the numbers of incident photons were determined by a calibrated Si photodiode.

The apparent quantum efficiency (AQE) was calculated by follow:

$$\text{AQE} = \frac{2 \times \text{Numbers of } \text{H}_2}{\text{Numbers of incident photons}} \times 100\%$$

$$= \frac{N_e}{N_p} \times 100\% = \frac{2 \times M \times N_A}{\frac{E_{total}}{E_{photon}}} \times 100\%$$

$$= \frac{2M \times N_A}{S \times P \times t} \times 100\% = \frac{2 \times M \times N_A \times h \times c}{S \times P \times t \times \lambda} \times 100\%$$

$$h \times \frac{C}{\lambda}$$

Where, M is the amount of H₂ molecules (mol), N_A is Avogadro constant (6.022×10²³/mol), h is the Plank constant (6.626×10⁻³⁴ J S), c is the speed of light (3×10⁸ m/s), S is the irradiation area (cm²), P is the intensity of irradiation light (W/cm²), t is the photoreaction time (s), λ is the wavelength of the monochromatic light (m).

And the parameters of the irradiation light used in this work were presented in the following table. Meanwhile, the photoreaction time in this work is 3600 s.

Table S1 The parameters of the irradiation light.

Wavelength (nm)	Light intensity (mW/cm ²)	Time (s)	Irradiation area (cm ²)
420	12.7	3600	23.75
435	7.24		
450	6.83		
475	5.63		
500	8.25		
520	10.32		
600	7.0		

Fig. S1 Enlarged XRD patterns of the obtained samples.

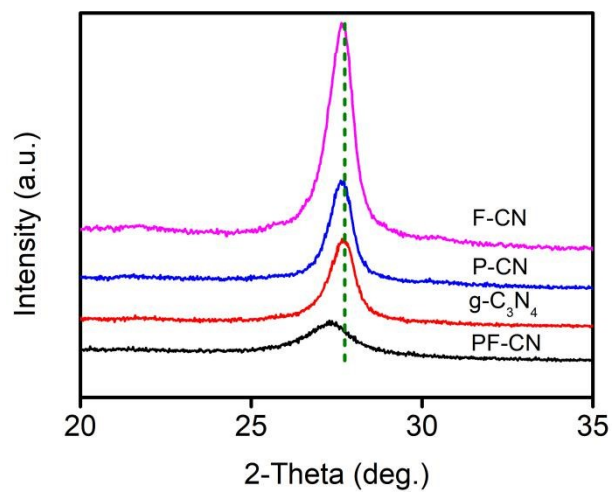


Fig. S2 TEM images of g-C₃N₄ (a), F-CN (b), P-CN (c) and PF-CN (d).

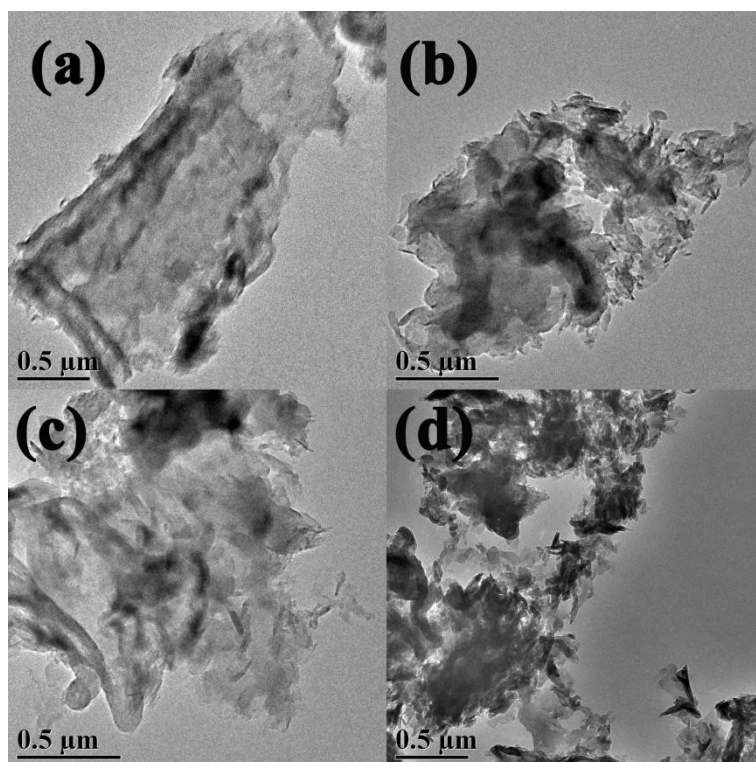
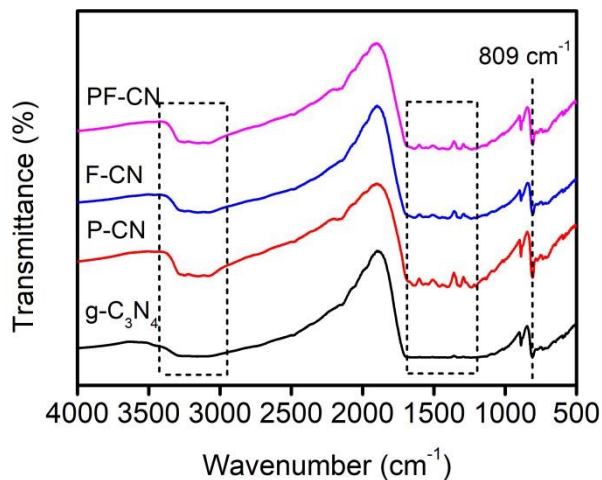


Fig. S3 FT-IR spectra of the as-prepared samples.



FT-IR spectroscopy was carried out to uncover the chemical structure of the obtained samples. The peak located at 809 cm⁻¹ was ascribed to the out-of-plane breathing vibration of tri-s-triazine heterocycles.¹ The peaks at 1200-1700 cm⁻¹ were mainly attributed to the characteristic stretching modes of aromatic CN heterocycles in g-C₃N₄.² The broad peaks located at 2900-350 cm⁻¹ corresponded to the amino (N-H) and hydroxyl (O-H) groups at surface. Clearly, the FT-IR spectra of P- or/and F-doped carbon nitride resembles g-C₃N₄ in the characteristic bands, indicating that the typical graphitic structure of carbon nitride was well maintained after doping heteroatom.

Fig. S4 XPS survey spectra of g-C₃N₄, F-CN, P-CN and PF-CN samples.

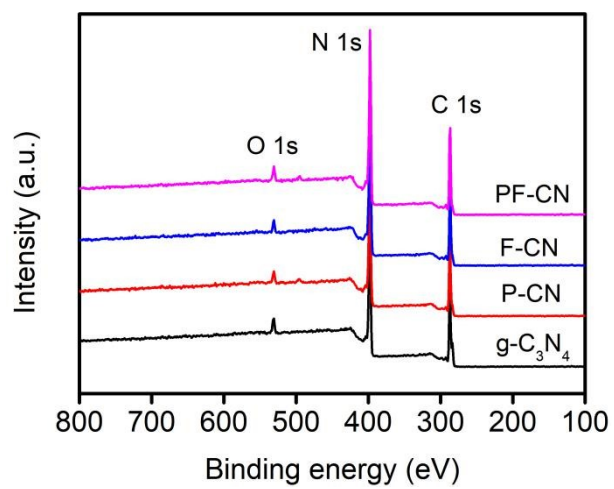


Table S2 The content of C, N, P and F elements in the obtained samples.

Sample	C (wt%)	N (wt%)	P (wt%)	F (wt%)
g-C ₃ N ₄	59.14	40.86	0	0
P-CN	63.25	36.55	0.52	0
F-CN	61.37	38.26	0	0.38
PF-CN	62.98	36.22	0.44	0.36

Fig. S5 The optical band gap of the obtained samples.

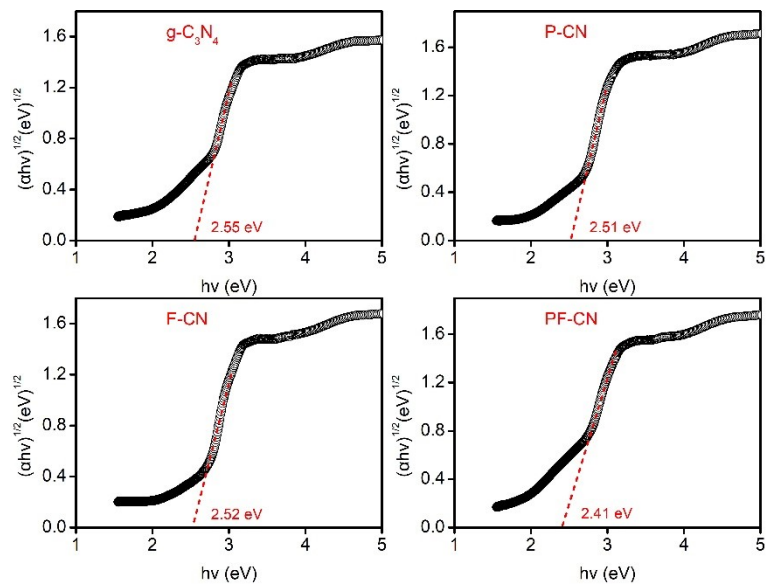


Fig. S6 Mott-Schottky plots of the prepared samples.

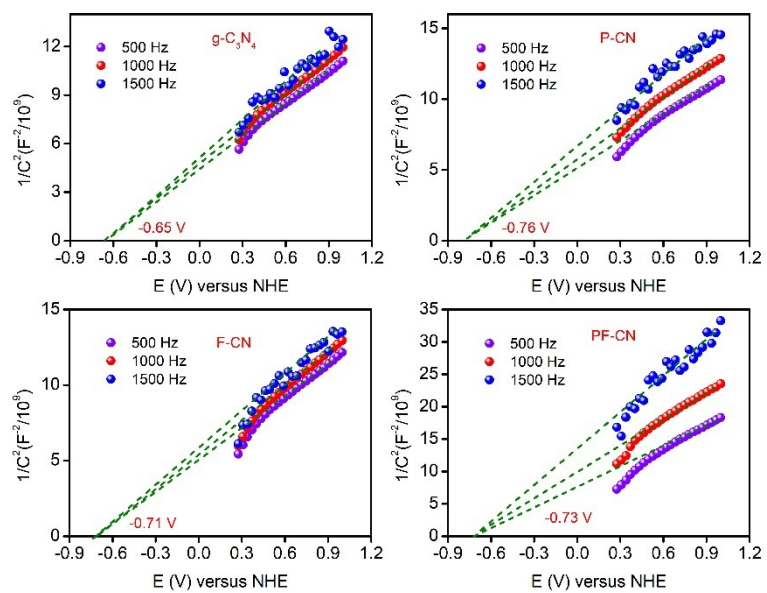


Fig. S7 Electronic structures of the obtained g-C₃N₄, P-CN, F-CN and PF-CN.

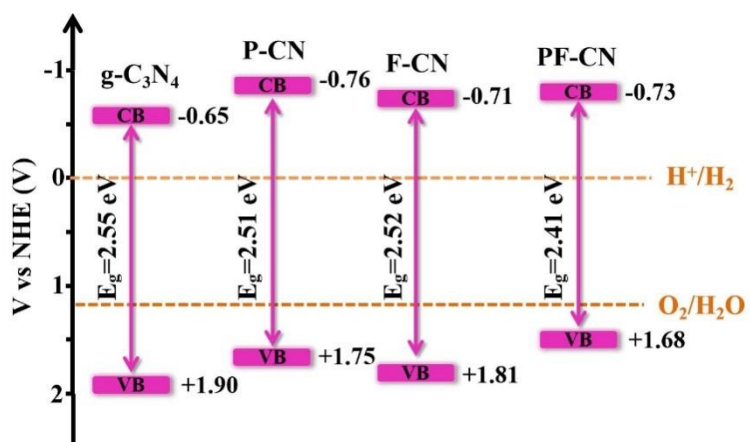


Fig. S8 Photocatalytic H₂ evolution performance over different concentration of P- (a) and F- (b) doped carbon nitride samples.

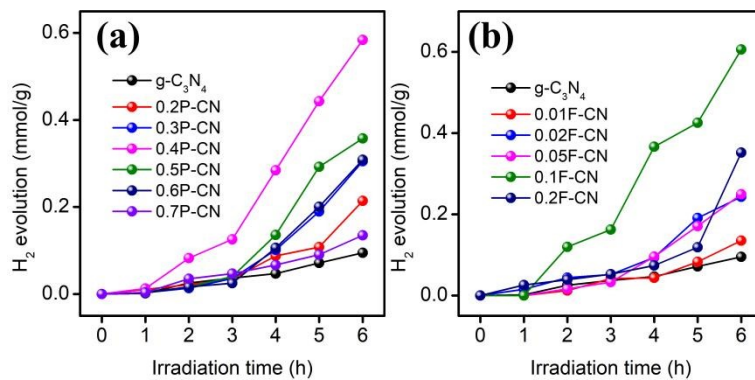


Fig. S9 Photocatalytic H₂ evolution performance over P- and F- co-doped carbon nitride samples.

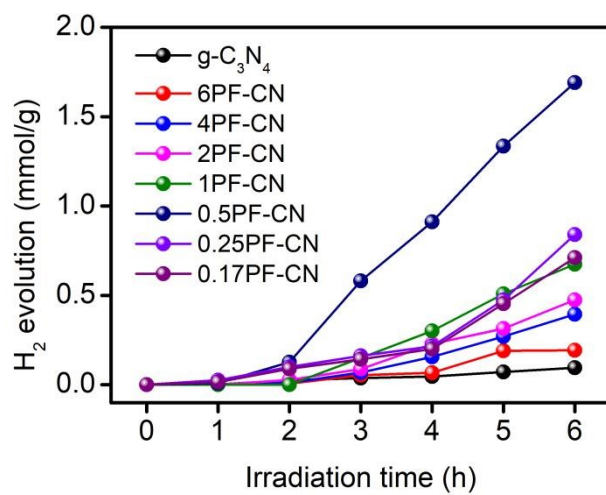


Fig. S10 Photocatalytic H₂ evolution performance under single-wavelength irradiation.

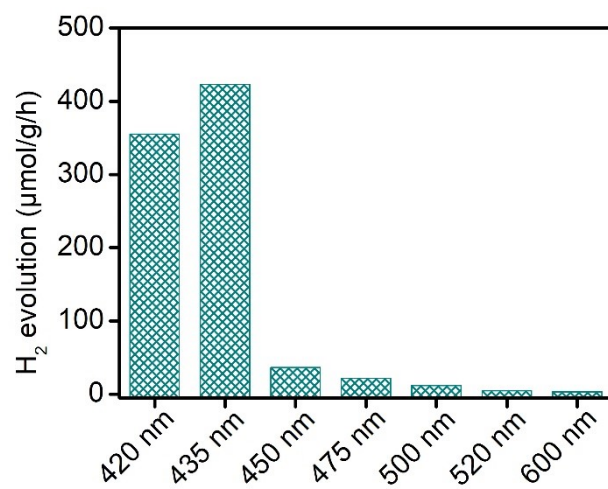


Table S3 Comparison of AQE of PF-CN with those of other catalysts reported in literature.

Entry	Catalysts	AQE (%)	Wavelength (nm)	Ref.
1	PF-CN	3.76	435	This work
2	CN-UDF	6.3	420	3
3	CCNS-50	~7.8	420	4
4	g-C ₃ N ₄ /graphene/MoS ₂	3.4	420	5
5	d-CNS	1.75	420	6
6	CN-10	2.2	420	7
7	p-CN ₂	0.79	420	8
8	P-DCN	1.46	420	9
9	NSNOCN	10.8	420	10
10	2.0wt.%Co(Mo-Mo ₂ C)/g-C ₃ N ₄	6.7	420	11
11	DSCN	1.2	420	12
12	CNP	6.79	420	13
13	CNA	5.07	420	14
14	Fe@g-C ₃ N ₄	6.89	420	15
15	MoS ₂ /g-C ₃ N ₄	3.33	410	16

Fig. S11 XRD of PF-CN before and after the cycling test.

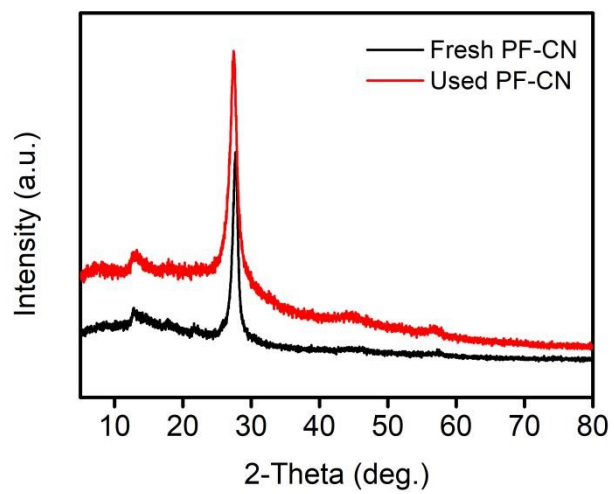
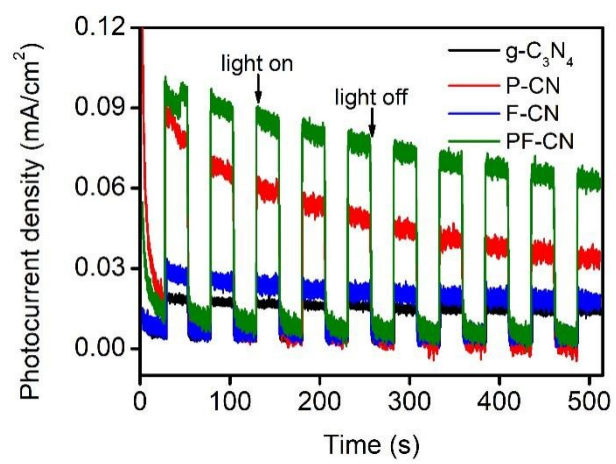


Fig. S12 The transient photocurrent response of the prepared samples.



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