Supporting Information

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# Doping-induced enhancement of crystallinity in polymeric carbon nitride nanosheets to improve the visible-light photocatalytic activity

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# **Experimental section**

## Materials

Urea (CO(NH<sub>2</sub>)<sub>2</sub>), sodium fluoborate (NaBF<sub>4</sub>), alcohol (C<sub>2</sub>H<sub>6</sub>O), isopropyl alcohol(C<sub>3</sub>H<sub>8</sub>O), para benzoquinone (BQ), sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>) and potassium hydroxide (KOH) are analytical grade and used directly without further treatment.

Preparation of photocatalysts

# Synthesis of pure CN

Pure CN was prepared by a thermal polymerization method. Typically, 15 g urea with 20 mL of DI water was placed into a 100 mL ceramic crucible with a cover. Then the crucible was heated in a muffle furnace at 550 °C for 2 h at a heating rate of about 5 °C min<sup>-1</sup>. Finally, the crucible was cooled naturally to room temperature, and CN powders with cream color were obtained.

Synthesis of CN-hot and CN-B/F nanosheets.

0.5 g of pure CN and a calculated mass of NaBF<sub>4</sub> were mixed and heated in a muffle furnace at 440 °C for 2 h at a heating rate of 5 °C min<sup>-1</sup>. The obtained pale yellow mixture was filtrated by washing with distilled water and finally dried at 60 °C overnight. The weight of NaBF<sub>4</sub> are 0, 0.1, 0.2 and 0.3g, and the resulting CN-B/F samples are denoted as CN-hot, CN-B/F-1, CN-B/F-2, CN-B/F-3, respectively.

# Characterization

The chemical structures of samples were determined by XRD to analysis the structure on

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Bruker with Cu K $\alpha$  radiation at 40 kV and 40 mA. FTIR spectra were recorded by an IR Affinity-1 FTIR spectrometer in the frequency 5 and range of 4000-450 cm<sup>-1</sup>. XPS spectroscopy was evaluated to estimate the binding energies on a Thermo Scientific ESCALAB 250 instrument using monochromated Al K $\alpha$  source with radiation at 250 W. SEM images were obtained with a Quanta 250FEG Field emission scanning electron microscope. UV-vis spectroscopy performed by a Varian Cary 5000 spectrophotometer. PL measurements were carried out using Edinburgh FL/FS900 spectrophotometer.

#### **Photoelectrochemical measurements**

The photoelectrochemical tests were performed on a CHI660E electrochemical workstation using a three-electrode system. An Ag/AgCl and a Pt plate were used as the reference and counter electrode, respectively. The prepared samples coated on FTO film as working electrode was located in 0.1 mol L<sup>-1</sup> Na<sub>2</sub>SO<sub>4</sub> aqueous electrolyte, which was chosen as the working electrode. The electrochemical impedance spectra (EIS) was carried out with the amplitude of the applied sine wave potential of 50 mV and a frequency ranging from 0.05 Hz to 100 kHz. The photocurrent response of the photocatalysts as light on and off was measured without bias voltage with a 55 W fluorescent lamp provided incident light. The Mott-Schottky (MS) plots were measured at a variety of frequency to determine band gap level.

Catalytic activity measurement

#### Degradation of MO, RhB, phenol and TC under visible light

The photocatalytic activity was evaluated by the degradation of methyl orange (MO), Rhodamine B (RhB) and phenol under a 300 W tungsten lamp as visible light source, and tetracycline hydrochloride (TC) with a 300 W Xe lamp with a 420 nm cutoff filter as visible light. Typically, MO, RhB and phenol (80 mL, 10 mg L<sup>-1</sup>) with samples (10 mg), and TC (80 mL, 30 mg L<sup>-1</sup>) with samples (50 mg) were mixed in a glass bottle in the dark with continuous ultrasound for 30 min at room temperature to reach the adsorption-desorption equilibrium between the dye and catalyst. During the photoreaction process, 5 mL mixture was collected in the 1 h intervals. Centrifugal supernatant liquor was measured using UV–vis spectroscopy (UV-5100, Anhui Wanyi) to record the maximum absorbance at 460 nm for MO, 550 nm for RhB, 270 nm for phenol and 360 nm for TC, respectively.

### The OER experiment

The OER experiment was performed on an electrochemical work station (CHI 660E) with a three-electrode setup in 1.0 M KOH solution by using a graphite rod as the counter electrode and Ag/AgCl electrode as the reference electrode. 1.5 mg photocatalyst loaded on nickel foam (NF) glass (1 cm × 1 cm) was chosen as the working electrode. Linear sweep voltammetry (LSV) was carried out with a scan rate of 20 mV s<sup>-1</sup>, and a 300 W tungsten lamp provided incident visible light. The recorded potentials were converted using the equation:  $E_{RHE} = E_{Ag/AgCl} + 0.059 \times pH + 0.197$ .



Figure S1. Zeta potential of CN, CN-hot, CN-B/F-1, CN-B/F-2 and CN-B/F-3.

S1.	Samplas	Ator	Atomic percentage atomic ratios				
	Samples	С	Ν	В	F	N/C	_
	CN	43.75%	56.25%	0	0	1.29	
	CN-B/F-2	42.98%	51.09%	5.31%	0.62%	1.19	

Summarized EDS data of C, N, B and F atom and surface N/C atom ratios of CN and CN-B/F-2.



Figure S2. XPS survey spectra for CN and CN-B/F-2.

**Table S2.** Summarized XPS data for CN and CN-B/F-2 surface N/C atom ratios determined from quantitative analyses are provided.

XP	S
samples	N/C
CN	1.48
B/F-CN	1.11

**Table S3.** Summarized XPS data for CN and CN-B/F-2 surface C, N, B and F atom ratios determined from quantitative analyses are provided.

XPS						
samples	С	N	В	F		
CN	41.29%	59.71%	0%	0%		
B/F-CN-0.2	45.32%	51.90%	1.92%	0.86%		

**Table S4.** Band positions of CN, CN-B/F-1, CN-B/F-2 and CN-B/F-3. All the values in tables are referenced to the electrochemical scale of the reversible hydrogen electrode.

Product	CB, eV (NHE)	VB, eV(NHE)	E <sub>g</sub> , eV
CN	-0.89	1.96	2.85
CN-B/F-1	-0.70	2.13	2.83
CN-B/F-2	-0.63	2.18	2.81
CN-B/F-3	-0.77	2.02	2.79



Figure S3. SEM-EDS elemental mapping of CN.

 Table S5. Comparison of photodegradation efficiency of CN-B/F-2 photocatalyst with another CN-based photocatalysts under visible light irradiation.

Photocatalyst	Photocatalyst	Light	Model	Initial	Photodegradation	Ref.
	dosage (mg)	source	pollutant	concentration	efficiency (h-1	
				(mg/L)	10mg <sup>-1</sup> )	
CN-B/F-2	10	300W,	МО	10	0.12	This
		Halogen				work
		lamp				
S doped CN	70	300W,	MO	11	0.03	1
		Halogen				
B doped CN	200	300 W	MO	4	0.012	2
		Xe lamp				
O doped CN	100	300W	MO	10	0.016	3
		Xe lamp				
$Al_2O_3/g$ - $C_3N_4$	100	350W	MO	10	0.046	4
		Xe lamp				
$MoO_3/g-C_3N_4$	100	350W	MO	10	0.106	5
		Xe lamp				
$Ag_2O/g$ - $C_3N_4$	100	250W	MO	10	0.083	6
		infrared				
		lamp				
$LaCoO_3/g$ - $C_3N_4$	50	300 W	MO	10	0.0415	7
		Xe-arc				
		lamp				
Ag <sub>2</sub> CrO <sub>4</sub> /g-	50	300 W	MO	10	0.082	8
$C_3N_4$		Xe-arc				
		lamp				
CN-B/F-2	10	300W,	RhB	10	0.54	This
		Halogen				work
		lamp				
						_
flake-like	100	300W	RhB	10	0.126	9
porous CN		Xe lamp				
P doped CN	50	250 W	RhB	10	0.077	10
		high-				

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		pressure				
		sodium				
		lamp				
O doped CN	100	300W	RhB	5	0.285	3
		Xe lamp				
Na/g-C <sub>3</sub> N <sub>4</sub>	50	250 W	RhB	10	0.077	11
		high-				
		pressure				
		sodium				
		lamp				
$Ka/g-C_3N_4$	50	250 W	RhB	10	0.132	12
		high-				
		pressure				
		sodium				
		lamp				
Ka-Na/g-C <sub>3</sub> N <sub>4</sub>	50	250 W	RhB	10	0.204	13
		high-				
		pressure				
		sodium				
		lamp				
[WO4] <sup>2–</sup> /g-	100	300 W	RhB	10	0.132	14
$C_3N_4$		Halogen				
		lamp				
	100					15
YVO <sub>4</sub> /g-C <sub>3</sub> N <sub>4</sub>	100	350W	RhB	10	0.234	15
		Xe lamp				10
TiO <sub>2</sub> /In <sub>2</sub> O <sub>3</sub> /g-	80	30W	RhB	10	0.345	16
$C_3N_4$		Xe lamp				
$C_{2}O_{2}/\alpha \subset N_{2}/N_{2}$	100	2011/	DhD	10	0.15	17
rGO	100	20 W Xe lamp	NIID	10	0.13	
100		AC Iamp				



**Figure S4.** a) Phenol (10 mg/L) degradation and b) the slope of degradation for (10 mg) CN and CN-B/F-2 under visible light. c) TC (30 mg/L) degradation and d) the slope of degradation for (50 mg) CN and CN-B/F-2 under visible light.

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