

Supporting Information Materials for

Multi-heteroatom doped Fe@CN activation peroxomonosulfate for the removal of trace organic contaminants from water: optimizing fabrication and performance

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Test S1 EPR and Electrochemical experimental procedures

ESR was used to qualitatively identify $\text{SO}_4^{\bullet-}$, $\cdot\text{OH}$, and $^1\text{O}_2$ in the reaction system. $\text{SO}_4^{\bullet-}$ and $\cdot\text{OH}$ were captured using the capture agent DMPO at a concentration of 88.0 mM, and $^1\text{O}_2$ was captured using the capture agent TEMP at a concentration of 14.2 mM. The experimental procedure was similar to the degradation experiments but without the addition of contaminants. 0.3 mL of the sample solution was mixed with 0.3 mL of the capture agent solution at 0, 5, 15, 30, 45, and 60 min after the start of the reaction, and then the samples were loaded and tested by capillary tube after mixing. The test conditions were as follows: scanning width of 100 G, microwave attenuation of 10 dB, modulation amplitude of 1.0 G, central magnetic field of 3521.45 G, microwave frequency of 9.856 GHz, microwave power of 4.0 mW, and scanning time of 80 s.

The working electrodes of FexCN-650, Fe@CN, P-Fe@CN, B-Fe@CN and PB-Fe@CN were prepared as follows (FexCN-650 was taken as an example): Add 0.010 g of FexCN-650 catalyst powder before reaction into 1.0 mL of anhydrous ethanol, add 0.05 mL of Nafion reagent to the above solution, and fully sonicate the catalyst to make it evenly dispersed. 10.0 μL of the dispersed solution was added dropwise onto the surface of a glassy carbon electrode (5 mm in diameter) and dried naturally for 12 h. The catalysts were used for the electrochemical analysis using an electrochemical workstation. An electrochemical workstation was used for electrochemical testing. A three-electrode system was constructed, with the prepared FexCN-650 electrode sheet

as the working electrode, the platinum wire electrode as the counter electrode, the silver/silver chloride electrode as the reference electrode, and the electrolyte as 0.05 mol/L Na_2SO_4 solution. The working parameters were set as follows: initial potential -2.0 V, voltage setting -2.0 V~2.5 V, scanning rate 10 mV/s, and CV curve was measured. The working parameters were set as follows: frequency 0.01~106 Hz, and the EIS curve was measured. Set the working parameters as: voltage setting -0.8 V~0.2V, scan rate 10 mV/s.

Table S1. Reagents and dosage for the preparation of X-C₃N₄ in ceramic crucibles

X-C ₃ N ₄	Adding dose of specific chemicals (g)				Fabrication parameters		
	C ₃ H ₆ N ₆	CH ₄ N ₂ S	H ₃ BO ₃	NH ₄ H ₂ PO ₄	Calcination temp. (°C)	Ramp rate (°C/min)	holding time (h)
g-C ₃ N ₄	10	-	-	-	550	5	4
S-C ₃ N ₄	4	2	-	-	550	5	4
B-C ₃ N ₄	5	-	0.62	-	500	10	1.5
SB-C ₃ N ₄	10	5	0.62	-	550	5	3
P-C ₃ N ₄	5	-	-	0.1	550	2	2
SP-C ₃ N ₄	10	5	-	0.2	550	2	2
PB-C ₃ N ₄	10	-	0.62	0.2	550	2	2
SPB-C ₃ N ₄	10	5	0.62	0.3	550	2	2

Table S2. The list of abbreviation

Abbreviated word or phrase	Full name
TOrCs	trace organic contaminants
SR-AOPs	sulfate radical advanced oxidation processes
MOFs	metal-organic frameworks
DIC	dicamba
ATL	atenolol
PMS	Peroxymonosulfate
DMF	N,N-dimethylformamide
DMPO	5,5-dimethyl-1-pyrroline N-oxide
TEMP	2,2,6,6-tetramethylpiperidine
g-C ₃ N ₄	Graphitic carbon nitride
SEM	scanning electron microscopy
XD	X-ray powder diffraction analyzer
XPS	X-ray photoelectron spectroscopy
CV	cyclic voltammetry
EIS	electrochemical impedance spectroscopy
TfL	Tafel
HPLC	high performance liquid chromatography
EPR	electron paramagnetic resonance spectrometer

Table S3. Diffraction angles and layer spacings corresponding to the (002) crystal planes of X-C₃N₄

X-C ₃ N ₄	g-C ₃ N ₄	S-C ₃ N ₄	P-C ₃ N ₄	B-C ₃ N ₄	SP-C ₃ N ₄	SB-C ₃ N ₄	PB-C ₃ N ₄	SPB-C ₃ N ₄
2θ (°)	27.6	27.58	27.42	26.74	27.579	27.18	27.459	27.6
d (nm)	0.323	0.323	0.325	0.331	0.323	0.328	0.325	0.323

Table S4. Elemental content of prepared X-Fe@CN by EDS analysis

[illegible]

Table S5. The predicted content of S, P and B without considering the losses during the preparation process

	S-Fe@CN	P-Fe@CN	B-Fe@CN	SP-Fe@CN	SB-Fe@CN	PB-Fe@CN	SPB-Fe@CN	Units
S	7.022	-	-	6.929	6.743	-	5.059	wt.%
P	-	0.264	-	0.177	-	0.249	0.170	wt.%
B	-	-	0.964	-	0.347	0.501	0.501	wt.%

Table S6. The element compositions of prepared FexCN-650, Fe@CN, P-Fe@CN, B-Fe@CN and PB-Fe@CN

Catalyst	C (at.%)	N (at.%)	O (at.%)	Fe (at.%)	P (at.%)	B (at.%)
FexCN-650	72.45	6.44	17.21	3.9	-	-
Fe@CN	71.29	9.14	16.62	2.94	-	-
P-Fe@CN	59.65	12.37	21.78	4.09	2.11	-
B-Fe@CN	63.56	7.99	19.2	3.02	-	6.24
PB-Fe@CN	58.04	8.59	20.64	3.71	1.4	7.63

Table S7. The relative content of C 1s species of prepared FexCN-650, Fe@CN, P-Fe@CN, B-Fe@CN and PB-Fe@CN

Catalyst	FexCN-650	Fe@CN	P-Fe@CN	B-Fe@CN	PB-Fe@CN
C-C (at.%)	44.31	46.67	39.18	37.11	39.42
C-N (at.%)	10.07	11.77	7.94	22.00	7.08
C-O (at.%)	13.75	5.23	10.56	4.45	4.27
N-C=N (at.%)	-	7.61	1.85	-	4.32
O-C=O (at.%)	4.32	-	0.13	-	2.95

Table S8. The relative content of Fe 2p species of prepared FexCN-650, Fe@CN, P-Fe@CN, B-Fe@CN and PB-Fe@CN

Catalyst	FexCN-650	Fe@CN	P-Fe@CN	B-Fe@CN	PB-Fe@CN
Fe ⁰ (at.%)	0.01	0.04	0.11	0.04	0.15
Fe ²⁺ 2p _{3/2} (at.%)	0.72	1.06	1.39	0.84	0.63
Fe ³⁺ 2p _{3/2} (at.%)	1.84	0.59	0.63	1.05	1.72
sat Fe ³⁺ (at.%)	0.08	0.28	1.09	0.19	0.27
Fe ²⁺ 2p _{1/2} (at.%)	0.55	0.53	0.55	0.57	0.28
Fe ³⁺ 2p _{1/2} (at.%)	0.61	0.32	0.23	0.18	0.55
sat Fe ²⁺ (at.%)	0.09	0.13	0.10	0.15	0.09

Table S9. The relative content of O 1s species of prepared FexCN-650, Fe@CN, P-Fe@CN, B-Fe@CN and PB-Fe@CN

Catalyst	FexCN-650	Fe@CN	P-Fe@CN	B-Fe@CN	PB-Fe@CN
Fe-O (at.%)	4.46	4.23	5.75	4.84	5.07
C=O (at.%)	5.83	4.61	10.83	7.75	5.93
C-OH (at.%)	2.15	2.63	3.15	3.63	5.78
Absorbed Oxygen (at.%)	4.76	5.15	2.05	2.99	3.86

Table S10. The relative content of N 1s species of prepared FexCN-650, Fe@CN, P-Fe@CN, B-Fe@CN and PB-Fe@CN

Catalyst	FexCN-650	Fe@CN	P-Fe@CN	B-Fe@CN	PB-Fe@CN
Pyridinic N (at.%)	3.17	3.77	2.59	2.17	1.70
Fe-N (at.%)	-	-	3.79	1.52	1.99
Pyrrolic N (at.%)	1.06	1.84	1.41	1.92	2.19
Quaternary N (at.%)	0.89	1.58	1.83	1.27	1.66
Graphite N (at.%)	0.53	0.45	2.09	0.82	1.05
N-O (at.%)	0.80	1.50	0.67	0.29	-

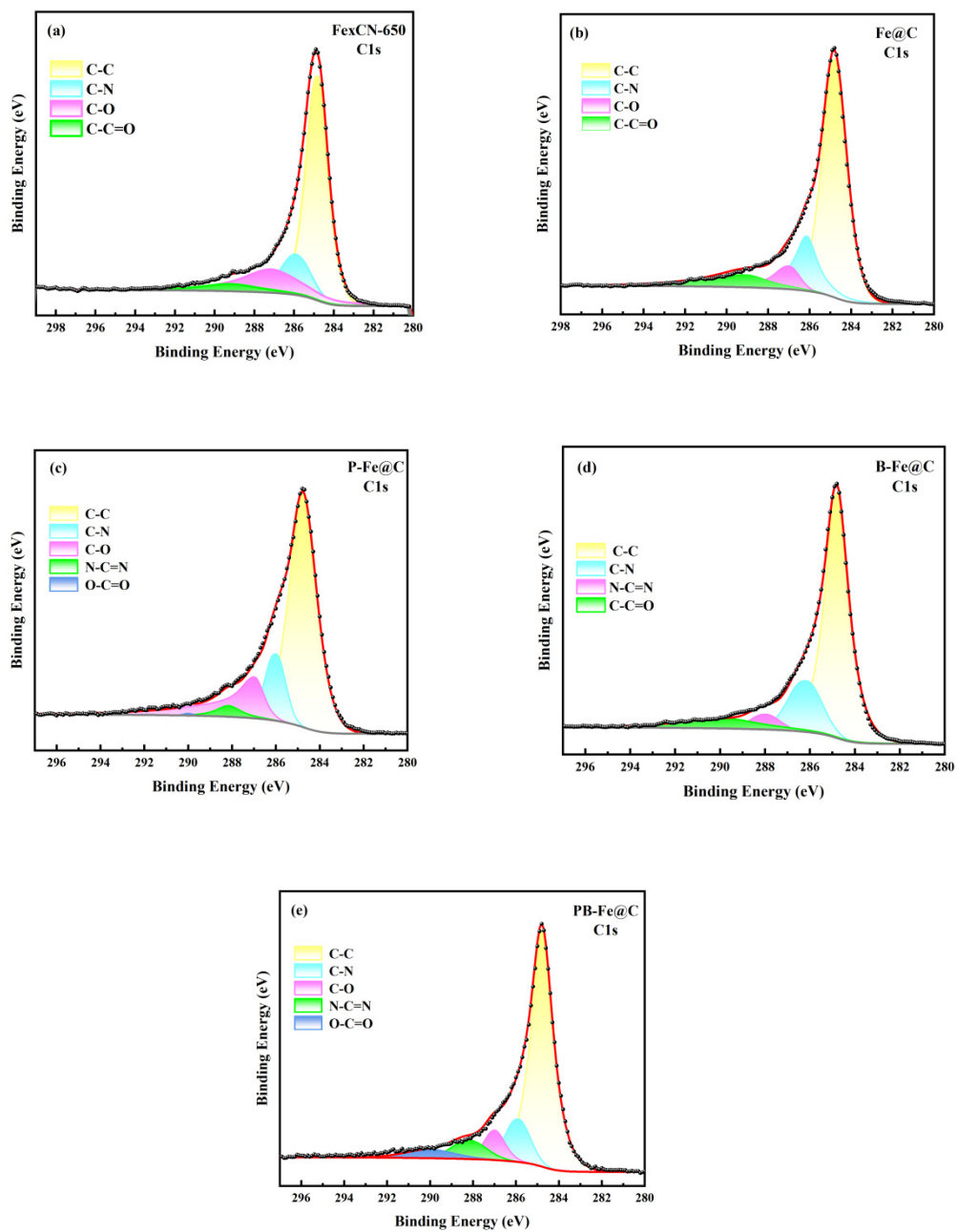


Figure S1. The C 1s high-resolution spectra of (a) FexCN-650, (b) Fe@CN, (c) P-Fe@CN, (d) B-Fe@CN and (e) PB-Fe@CN.

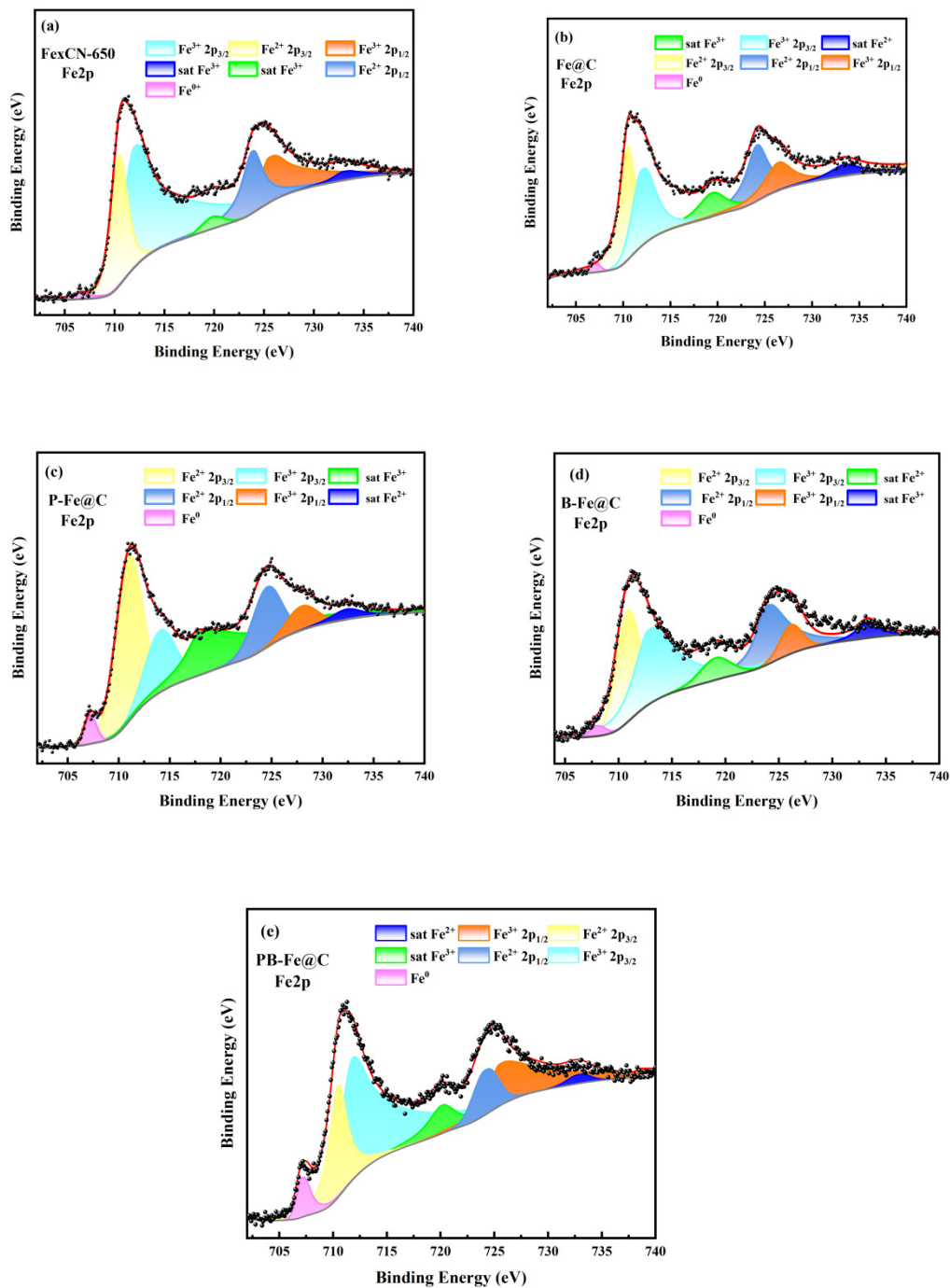


Figure S2. The Fe 2p high-resolution spectra of prepared (a) FexCN-650, (b) Fe@CN, (c) P-Fe@CN, (d) B-Fe@CN and (e) PB-Fe@CN.

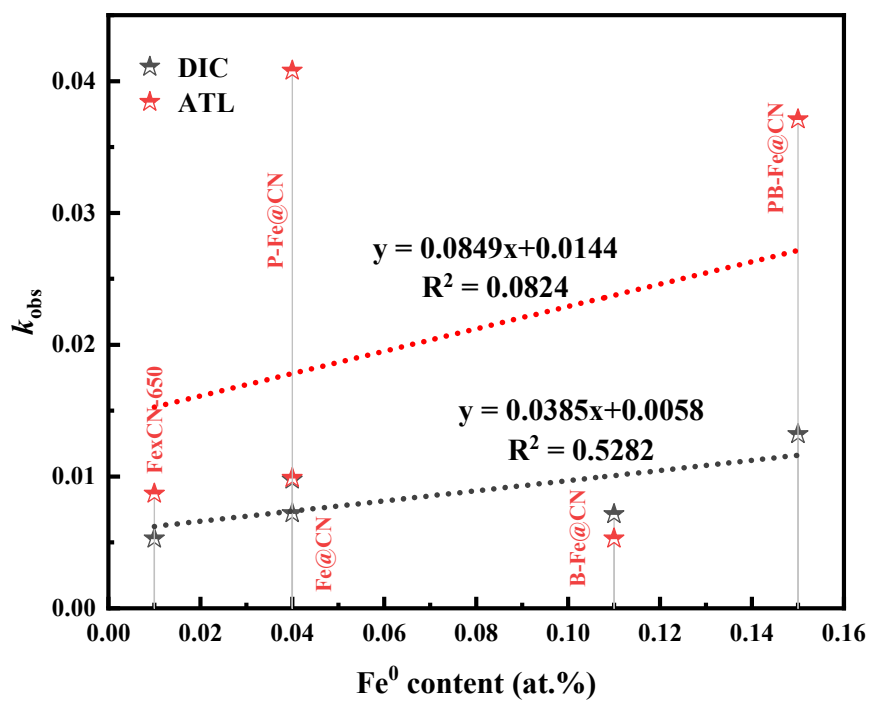


Figure S3. The correlation of k_{obs} of DIC and ATL removal to Fe^0 content.

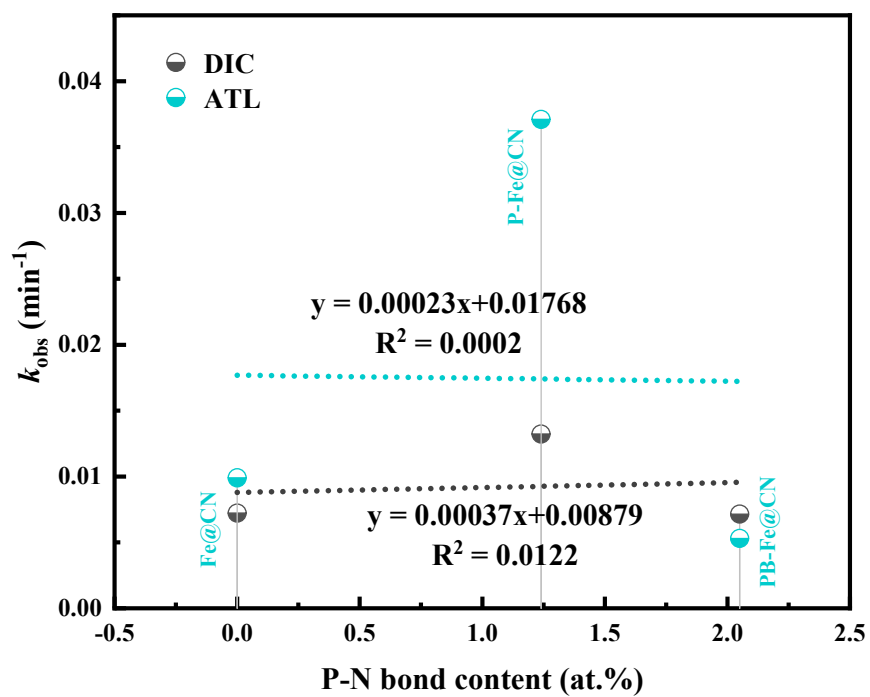


Figure S4. The correlation of k_{obs} of DIC and ATL removal to P-N bond content.

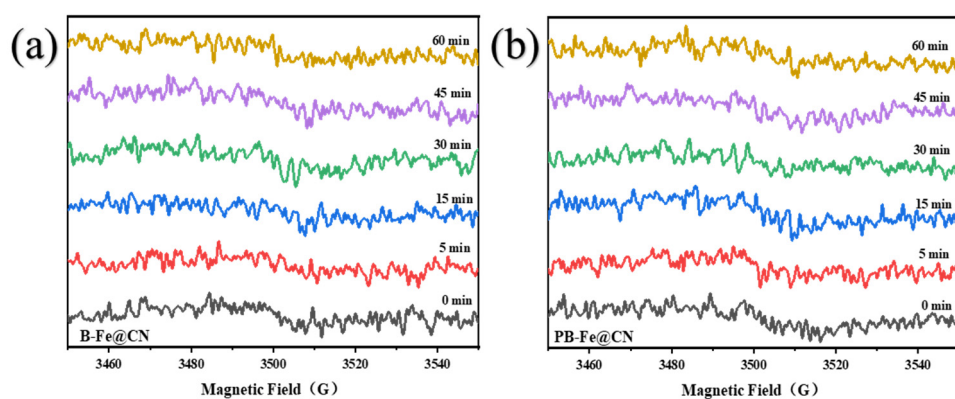


Figure S5. EPR spectra obtained using DMPO as spin-trapping agents in anhydrous ethanol

Experimental conditions: [PMS] = 1.30 mM, [B-Fe@CN] = 200 mg/L, [PB-Fe@CN] = 400 mg/L, initial pH = 7.0.