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Supplementary Information

High-coordinated Fe-N₅ sites effectively promoted peroxymonosulfate

activation for degradation of 4-chlorophenol

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1. Electrochemical Measurements

The electrochemical workstation (CHI 760E, Chenhua Instrument Co., China), utilizing a threeelectrode configuration, was employed for the assessment of electrochemical impedance spectroscopy (EIS), linear sweep voltammetry (LSV), and current-time (i-t) graphs. The catalysts were coated on the glass carbon electrode (GCE) as the working electrode. Pt and Ag/AgCl electrodes were used as the counter and reference electrodes, respectively. The preparation steps for the catalyst-modified GCE involved dispersing 10 mg of the catalyst into a mixed solution of 0.2 mL Nafion (5%), 0.1 mL isopropanol, and 2.7 mL deionized water (DI). After 30 min of ultrasonic treatment, 5 µL of the resulting homogeneous catalyst ink was dripped onto the surface of the GCE. Before each test, the GCE was repeatedly polished with alumina slurries on a felt pad, followed by rinsing with DI water and dripping of catalyst ink on the GCE. The catalyst's EIS was measured using an electrolyte consisting of 50 mL of 4-CP solution (20 mg L⁻¹) within a sweep range of 1×10⁻² to 1×10⁶ Hz. For LSV and i-t measurements, 200 mmol L⁻¹ boric acid buffer was used as the electrolyte. The current at the working electrode was recorded by sweeping the potential from 0.2 to 1.4 V at a scan rate of 10 mV s^{-1} . Additionally, i-t curves for the Fe-N₅ electrode were acquired at 0.5 V vs. Ag/AgCl.

2. Determination of PMS consumption

The concentration of PMS remaining in the solution was determined by the colorimetric method. A reaction sample of 0.1 mL was collected and filtered through a 0.22 μ m filter. Later, 0.4 mL ABTS (10 mM), 0.2 mL Co²⁺ (10 mM), and 9.4 mL DI water were immediately added into the above sample to react for 10 min. A green-colored ABTS radical cation was formed. The resulting solution was analyzed by UV/Vis spectrophotometer (UV1800, Shimadzu, Japan) at the maximum absorbance wavelength of 735 nm.^[1]

3. Mathematical Formulations and Calculations

The pseudo-first order kinetic rate constant (k) of the degradation was calculated as follows:

$$-\ln(\frac{C_t}{C_0}) = kt$$

Where, C₀ and C_t represent the initial and the instant concentration of 4-CP.

The turnover frequency of the degradation was calculated as follows:

$$TOF = \frac{k}{[catalyst]_0}$$

Where, k wass the rate constant of the reaction, and $[Catalyst]_0$ was the loading of the catalyst.

4. Radical Probe Experiments

In this study, the steady-state concentration of SO_4 , OH, O_2 , and 1O_2 in the Fe-N₅/PMS system were be calculated using BA, NB, *p*-CBA, and FFA as probe compounds. Since the probe compounds were low concentration compared to 4-CP (20 mg/L for 4-CP, 2 mg/L for BA, NB, FFA and *p*-CBA), which would not affect 4-CP degradation. ^[2] The second-order reaction rate constants between organic compounds and reactive species (M⁻¹·s⁻¹) were shown in Table S6. The calculation methods of steady-state concentration of OH, SO_4 , 1O_2 , O_2 , $^-$ are as follows:

$$(k_{BA,OH} [OH]_{ss} + k_{BA,SO_4} [SO_4]_{ss})t = k_{BA}t$$
(1)

$$(k_{NB,OH} [OH]_{ss} + k_{NB,SO_4} [SO_4^{--}]_{ss})t = k_{NB}t$$
(2)

$$(k_{p-CBA,OH} [OH]_{ss} + k_{p-CBA,SO_4} [SO_4]_{ss} + k_{pCBA,1O_2} [1_{O_2}]_{ss} + k_{p-CBA,O_2} [O_2]_{ss} + k_{p-CBA,O_2}$$

$$(k_{FFA, OH} \cdot [OH]_{ss} + k_{FFA, SO_4} - [SO_4^{--}]_{ss} + k_{FFA, 1O_2} [1_{O_2}]_{ss} + k_{FFA, O_2} - [O_2^{--}]_{ss})t$$

$$= k_{FFA}t$$
(4)
$$k_{BA, OH} \cdot k_{BA, SO_4} - k_{NB, OH} \cdot k_{NB, SO_4} - k_{p-CBA, OH} \cdot k_{p-CBA, SO_4} - k_{pCBA, 1O_2},$$

$$k_{p-CBA, O_2} - k_{FFA, OH} \cdot k_{FFA, OH} \cdot k_{p-CBA, OH} \cdot k_{p-CBA, SO_4} - k_{pCBA, 1O_2},$$

 k_{FFA, SO_4} , $k_{FFA, 1O_2}$, k_{FFA, O_2} , values were taken from [2-3].

The pseudo-first order reaction rate constant ($k_{, BA}$, $k_{, NB}$, $k_{, p-CBA}$, $k_{, FFA}$) could be obtained from

the slope of the plots of $-ln\frac{[BA]}{[BA]_0}$, $-ln\frac{[NB]}{[NB]_0}$, $-ln\frac{[p-CBA]}{[p-CBA]_0}$, and $-ln\frac{[FFA]}{[FFA]_0}$, respectively. Then, the steady-state concentration of the reactive species was obtained by solving the equations 1-4 and was shown in Table S6.

5. Preparation of Fe-N₄ SAC

In the synthesis of Fe-N₄, 81.1 mg of FeCl₃·6H₂O and 2.59 g of ZnCl₂ were dissolved in 200 mL of formamide solution, and was stirred continuously for 45 min to achieve a homogeneous solution. This solution was heated at 180 °C for 12 h in a Teflon-lined autoclave. After cooling to room temperature, the resultant precipitate was centrifuged for 10 minutes and, washed with ethanol and DI water. The washed precipitate was then dried in an oven at 60 °C for 24 h. The dried powder was subsequently calcined at 900 °C with a rate of 5 °C min⁻¹ for 1 h under N₂ atmosphere, to obtain Fe-N₄ SAC.

E.

HPLC operating conditions for analyzing the pollutants.

Pollutants	Wavelength	Mobile phase (v/v)
2-CP	275	Water : Methanol=40:60
4-CP	280	Water : Methanol=40:60
2,4-DCP	280	Water : Acetonitrile=30:70
2,4,6-TCP	284	Water : Methanol=30:70
ВРА	230	Water : Methanol=30:70
Phenol	270	Water : Methanol=35:65
2-NP	280	Water : Methanol=20:80
4-NP	280	Water : Methanol=20:80
SDZ	265	Water : Acetonitrile =15:85
SMT	175	Water : Methanol=55:45

NB	265	Water : Acetonitrile=50:50
ВА	227	Water : Acetonitrile=50:50
FFA	214	Water : Acetonitrile=50:50
р-СВА	239	Water : Acetonitrile=50:50

EXAFS fitting parameters at the Fe K-edge for various samples (S_0^2 =0.820).

Sample	Shell	CNª	R(Å)⁵	σ²(Ų) ^c	ΔE ₀(eV) ^d	R factor
Fo foil	Fe-Fe	8*	2.474±0.00 3	0.0052±0.0 003	6 0+0 7	0.0010
Fe foll	Fe-Fe	6*	2.854±0.00 5	0.0068±0.0 007		0.0019
	Fe-O	3.4±0.3	1.938±0.01 7	0.0053±0.0	-5.2±2.1	0.0071
	Fe-O	2.7±0.4	2.103±0.02 9	020		
Fe ₂ O ₃	Fe-Fe	5.2±0.6	2.960±0.00 9		065±0.0 009 -3.3±1.4	
	Fe-Fe	4.2±0.8	3.381±0.01 1	0.0065±0.0 009		
	Fe-Fe	5.4±0.3	3.692±0.01 0			
Fe-N ₅	Fe-N	5.2±0.4	2.002±0.02 0	0.0043±0.0 028	-1.1±3.8	0.0025

Flow rate of mobile phase using 1.0 mL min⁻¹ for all experiments. was fixed to 0.820, according to the experimental EXAFS fit of Fe foil by fixing *CN* as the known crystallographic value. * This value was fixed during EXAFS fitting, based on the known structure of Fe. Fitting range: $3.0 \le k$ (/Å) ≤ 14.0 and $1.0 \le R$ (Å) ≤ 3.0 (Fe foil), $3.0 \le k$ (/Å) ≤ 13.8 and $1.0 \le R$ (Å) ≤ 4.0 $(Fe_2O_3), 2.0 \le k (/Å) \le 10.0 \text{ and } 1.0 \le R (Å) \le 2.5 (Fe-N_5).$ A reasonable range of EXAFS fitting parameters: 0.700 < $S_0^2 < 1.000, CN > 0, \sigma^2 > 0 Å^2, |\Delta E_0| < 10 \text{ eV}, R \text{ factor } < 0.02.$

Catalysts	4-CP (mg L ⁻¹)	PMS (mM)	Catalyst (g L ⁻¹)	k (min ⁻¹)	TOF (L (min·g)⁻¹)	Reference
Fe-N₅	20	0.33	0.05	2.99	59.8	This work
HFeNC-g-C ₃ N ₄	1	1	0.03	0.038	1.272	[4]
PSBC	10	1	0.4	1.7	4.25	[5]
MnN ₅	10	1	0.5	0.51	1.02	[6]
SAFe-OCN	12	1	0.5	0.21	0.42	[7]
γ-MnOOH	50	4	0.17	0.068	0.401	[8]
γ-Fe ₂ O ₃	20	0.5	0.2	0.15	0.745	[9]
FeMn@NCNT	6	1.6	0.1	1.266	12.66	[10]
Fe ₂ O ₃ -CoFe ₂ O ₄	10	2	0.01	0.147	14.7	[11]
Fe/Fe ₃ O₄@CPPy	2	0.25	0.08	0.392	4.9	[12]

Table S3

Comparison of reaction conditions and reaction parameters over the reported SACs and nanocatalysts for 4-CP degradation by PMS activation in the Fenton-like reaction.

Fe-MOF@Mn ₂ O ₃	10	2	0.2	0.086	0.43	[13]
BFA-500	3	0.5	0.05	0.0885	1.77	[14]

Parameters of the obtained water samples.

	Tap Water	River water	Reclaimed water
рН	7.65	7.40	8.34
HCO ₃ ⁻ (mg L ⁻¹)	28.82	63.60	44.14
SO ₄ ²⁻ (mg L ⁻¹)	41.63	90.65	21.90
PO ₃ ^{4−} (mg L ⁻¹)	0	0.13	0.01
NO_{3}^{-} (mg L ⁻¹)	0.46	8.94	49.91
Cl ⁻ (mg L ⁻¹)	12.23	94.63	55.71
TOC (mg L ⁻¹)	-	3.15	4.64

Comparison of k over the reported SACs and nanocatalysts for 2-CP, 2,4-DCP, and 2,4,6-TCP degradation.

Catalyst	<i>k</i> (min ⁻¹)	Reference			
2-CP					
Fe-N ₅	2.12	This work			
Fe-doped CeO ₂	0.0039	[15]			
TNTs@AC	0.044	[16]			
Zn1–xCdxS	0.037	[17]			
Fe-NZ	0.016	[18]			
2,4 DCP					
Fe-N ₅	2.04	This work			
Fe-Pd@ZIF-8	0.0785	[19]			
Cu ₂ S/Cu ₂ O nZVI	0.0143	[20]			
Ethylenediamine-N,N- disuccinic-acid (EDDS)	0.0414	[21]			
Organobentonite-nZVI	0.247	[22]			
2,4,6 ТСР					
Fe-N₅	1.83	This work			
ZVCow	1.40	[23]			
Zero-valent iron (ZVI)	0.087	[24]			
NiO/Al ₂ O ₃ catalyst	0.044	[25]			
Nanoscaled Fe ₃ O ₄ /CeO ₂	0.046	[26]			

Reactive species	Steady-state concentration (M)	ROS (%)
•ОН	2.46 × 10 ⁻¹³	11.70
SO4	1.09 × 10 ⁻¹³	5.2149
¹ O ₂	1.74 × 10 ⁻¹²	82.5056
0 ₂	1.22 × 10 ⁻¹⁴	0.5785

The steady-state concentrations and the contribution ratio of reactive species.



Figure S1. XRD patterns of Fe-N₄ and Fe-N₅.



Figure S2. (a) XPS survey spectra, (b) N1s, (c) Fe2p, and (d) C1s of Fe- N_4 and Fe- N_5 .



Figure S3. 4-CP adsorption on various catalysts in heterogeneous Fenton-like reaction. Reaction condition: [4-CP]₀=20 mg L⁻¹, [Catalyst]₀=0.05 g L⁻¹, [PMS]=0.2 g L⁻¹, pH=7.0, T=25 °C, adsorption time=30 min.



Figure S4. TOC removals in Fe-N₅/PMS system for various CPs. Reaction condition: $[4-CP]_0=[2-CP]_0=[2,4-DCP]_0=[2,4,6-TCP]_0=20 \text{ mg L}^{-1}$, $[Catalyst]_0=0.05 \text{ g L}^{-1}$, $[PMS]=0.2 \text{ g L}^{-1}$, pH=7.0, T=25 °C.



Figure S5. PMS consumption with various catalysts for 4-CP degradation. Reaction condition: $[4-CP]_0=20 \text{ mg } L^{-1}$, $[Catalyst]_0=0.05 \text{ g } L^{-1}$, $[PMS]=0.2 \text{ g } L^{-1}$, pH=7.0, T=25 °C.



Figure S6. Comparison of (a) k and (b) TOF of the reported SACs and nanocatalysts for 4-CP degradation by PMS activation.



Figure S7. Stability test of Fe-N₅ for 4-CP degradation. Reaction condition: $[4-CP]_0=20$ mg L⁻¹, $[Catalyst]_0=0.05$ g L⁻¹, [PMS]=0.2 g L⁻¹, pH=7.0, T=25 °C, reaction time=30 min.



Figure S8. Effect of pH on the 4-CP adsorption in Fe-N₅/PMS system. Reaction condition: $[4-CP]_0=20$ mg L⁻¹, $[Catalyst]_0=0.05$ g L⁻¹, [PMS]=0.2 g L⁻¹, pH=7.0, T=25 °C, adsorption time=30 min.



Figure S9. Degradation of various pollutants in Fe-N₅/PMS system. Reaction condition: $[BPA]_0=[Phenol]_0=[SDZ]_0=[SMT]_0=[2-NP]_0=20 \text{ mg } L^{-1}$, $[Catalyst]_0=0.05 \text{ g } L^{-1}$, $[PMS]=0.2 \text{ g } L^{-1}$, pH=7.0, T=25 °C.





Figure S11. (a) NB, (b) BA, (c) FFA, and (d) *p*-CBA degradation efficiency in Fe-N₅/PMS system. Reaction condition: Reaction condition: $[4-CP]_0=20 \text{ mg } L^{-1}$, $[Catalyst]_0=0.05 \text{ g } L^{-1}$, $[PMS]=0.2 \text{ g } L^{-1}$, pH=7.0, T=25 °C , $[probe]_0 = 2.0 \text{ mg } L^{-1}$.



Figure S12. *k* of NB, BA, FFA, and *p*-CBA degradation efficiency in Fe-N₅/PMS system. Reaction condition: $[4-CP]_0=20 \text{ mg L}^{-1}$, $[Catalyst]_0=0.05 \text{ g L}^{-1}$, $[PMS]=0.2 \text{ g L}^{-1}$, pH=7.0, T=25 °C, $[probe]_0=2.0 \text{ mg L}^{-1}$.



Figure S13. Effect of SCN⁻ on the 4-CP degradation in Fe-N₅/PMS system. Reaction condition: $[4-CP]_0=20 \text{ mg L}^{-1}$, $[Catalyst]_0=0.05 \text{ g L}^{-1}$, $[PMS]=0.2 \text{ g L}^{-1}$, pH=7.0, T=25 °C, $[SCN^-]=7.8 \text{ mM}$.



Figure S14. Effect of KI on the 4-CP degradation in FeN₅/PMS system. Reaction condition: $[4-CP]_0=20$ mg L⁻¹, $[Catalyst]_0=0.05$ g L⁻¹, [PMS]=0.2 g L⁻¹, pH=7.0, T=25 °C, [KI]=20 mM.



Figure S15. Linear sweep voltammetry obtained by $Fe-N_5$ as working electrode in the presence of PMS and 4-CP.



Figure S16. 2-D electron density distribution structure of (a) Fe-N $_4$ and (b) Fe-N $_5$.



Figure S17. PDOS of Fe-N₄ and Fe-N₅.



Figure S18. Free energy of 4-CP degradation in $\mbox{Fe-}N_4$ and $\mbox{Fe-}N_5.$

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