Duet Fe_3C and FeN_x Sites for H_2O_2 Generation and Activation toward Enhanced Electro-Fenton Performance in Wastewater Treatment

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The supporting information includes:

12 Pages

4 Texts

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Text S1 Calculation of TOC removal rate and rate constant of 2-CP

The TOC removal rate was calculated by the following eq. S1:

$$TOC\ removal\ rate(\%) = \frac{TOC_0 - TOC_t}{TOC_0} \times 100\% \qquad (S1)$$

where TOC_0 and TOC_t represent the TOC values at initial and reaction time (t), respectively.

A graph of ln([2-CP]$_0$/[2-CP]$_t$) versus time t would give a straight line with a slope as k_{app} (eq. S2),

$$\mathrm{Ln}\left(\frac{[2-CP]_0}{[2-CP]_t}\right) = k_{app} \times t \qquad (S2)$$

where [2-CP]$_0$ and [2-CP]$_t$ are the respective concentrations of 2-CP at initial and reaction time (*t*).

Text S2 Linear sweep voltammetry (LSV) measurement of Fe-based catalysts.

About 5 mg sample was dispersed in 0.5 mL suspension including water, isopropanol and Nafion solution (5 wt%) (215**:**273.5:10.75). The mixture was immersed in an ultrasonic bath for 30 min to prepare a homogeneous ink. The working electrode was prepared by deposition of 10 μl catalyst ink onto a Glassy carbon electrode (diameter: 3 mm). Hg/Hg_2Cl_2 and Pt wire were used as reference and counter electrodes respectively. LSV measurements were performed in the electrolyte of 0.05 M Na_2SO_4 at pH =7.0. The sweep speed equals 10 mV/s.

Text S3 Illustration of the calculation on the inhibition efficiency rate induced by quenching agents.

The inhibited efficiency rate was calculated according to the following equation (S3):

$$Inhibited\ \ efficiency\ rate(\%) = \frac{(k_{app} - k_{app.quenched})}{k_{app}} \times 100\% \qquad (S3)$$

where $k_{app}$and $k_{app.quenched}$ represent the original constant rate of the degradation and the value after quenched by scavengers, respectively.

Text S4 DFT calculations of H_2O_2 adsorption on FeN and Fe_3C particles.

The density functional theory (DFT) calculations were further performed to understand the interactions between H_2O_2 and Fe-N_x sites and Fe_3C particles. The structure models of FeN and Fe_3C were obtained based on the data of matched PDF card (JCPDS NO. 50-1087) and (JCPDS NO. 35-0772) as shown in Figure S12 and the corresponding results of the adsorption parameters were listed in Table S6.

Table S1 HPLC analytical methods of chlorophenols.

Chemical name	Mobile phase Methanol/%	Mobile phase Water/%	Flow rate /mL·min^{-1}	Wavelength/nm
2-CP	70	30	1	225
3-CP	70	30	1	225
4-CP	70	30	1	225
2,4-DCP	70	30	1	225
2,4,6-TCP	70	30	0.8	296

Table S2 Textural parameters of the as-prepared catalysts.

Sample	S_{BET}($m^2 \cdot g^{-1}$)	Pore Volume($cm^3 \cdot g^{-1}$) total	Pore Volume($cm^3 \cdot g^{-1}$) mesoporous volume	Average pore diameter(nm)
NC	21.5	0.027	0.025	5.0
Fe_3C@C	278	0.196	0.122	2.8
FeNC@C	298	0.212	0.129	2.8

Table S3 ^{57}Fe Mössbauer fitted parameters of Fe-based catalysts.

Catalyst		IS (mm·s^{-1})	QS (mm·s^{-1})	H (kOe)	W (mm·s^{-1})	Phase	Spectral contribution (%)	Ref. No.
FeNC@C	D1	0.28	0.95	-	0.35	$Fe^{III}N$	21.0	1
	S1	0.33	-0.02	488.4	0.31	A site in Fe_3O_4	4.8	2
	S2	0.53	0.02	430.7	0.65	B site in Fe_3O_4	3.3	2
	S3	-0.03	0.00	326.0	0.14	Fe^0	6.4	1
	S4	0.20	0.02	205.8	0.15	Fe_3C	35.7	3
	S5	0.18	-0.01	195.0	0.35	χ-Fe_5C_2(III)	24.7	4
	S6	0.24	-0.17	118.1	0.19	χ-Fe_5C_2(III)	4.1	4
Fe_3C@C	D2	0.29	0.92	-	0.45	Fe^{3+}	15.3	3
	S4	0.20	0.01	205.9	0.20	Fe_3C	84.7	3

Experimental uncertainties: isomer shift: IS±0.01 mm · s^{-1}; quadrupole splitting: QS±0.01 mm · s^{-1}; line width: W±0.01 mm · s^{-1}; spectral contribution:±0.5%.

Table S4 Relevant parameters of 2-CP degradation kinetics in the heterogeneous EF system under different conditions.

Catalysts	Initial pH	Quenched reagent	k_{app}/min^{-1}	R^2
FeNC@C	3.0	none	0.0714	0.9913
FeNC@C	7.0	none	0.0365	0.9754
FeNC@C	3.0	TBA	0.0185	0.9332
FeNC@C	7.0	TBA	0.0138	0.9054
FeNC@C	3.0	DMSO	0.0357	0.9037
FeNC@C	7.0	DMSO	0.0128	0.9300
FeNC@C	3.0	TBA&DMSO	0.002	0.9632
FeNC@C	7.0	TBA&DMSO	0.002	0.8903
FeNC@C	3.0	Sodium citrate	0.0359	0.9946
FeNC@C	7.0	Sodium citrate	0.0275	0.988
FeNC@C	3.0	1,10-phenanthroline	0.0555	0.9096
FeNC@C	7.0	1,10-phenanthroline	0.031	0.9450
FeNC@C	3.0	SCN^-	0.002	0.9760
FeNC@C	7.0	SCN^-	0.006	0.9231
Fe_3C@C	3.0	none	0.0254	0.9521
Fe_3C@C	7.0	none	0.0202	0.9040

Table S5 Relevant parameters of 2-CP degradation in practical effluents.

Sample	[HCO_3^-]10^{-3} mol/L	pH	TOC(mg/L)	IC(mg/L)	Conductivity（us/cm）	Degradation Efficiency
Yangtze river	1.1	7.88	4.68	22.36	357	85.4%
Secondary sedimentation tank	1.1	8.10	19.60	24.60	820	90.1%

Table S6 DFT results of H_2O_2 adsorbed on the surface of Fe_3C@C and FeN@C in the FeNC@C catalyst.

	O-O (Å)	O-H (Å)	O-Fe (Å)	$E_{ads}(H_2O_2)$(eV)
H_2O_2 single	1.47	0.98	-	-
H_2O_2 adsorbed on FeN	1.98	0.98	1.84	-0.35
H_2O_2 adsorbed on Fe_3C	1.51	0.99	2.13	-0.29

Table S7 H_2O_2 concentrations generated in 120 min from different catalysts under various conditions in HEF system.

Sample	pH3.0/mM	pH7.0/mM
blank	0.46	0.25
Fe_3C@C	1.08	0.51
FeNC@C	0.40	0.22
NC	0.60	0.37
Fe_3C@C-SCN	1.28	0.64
FeNC@C-SCN	1.50	0.81
NC-SCN	0.74	0.45

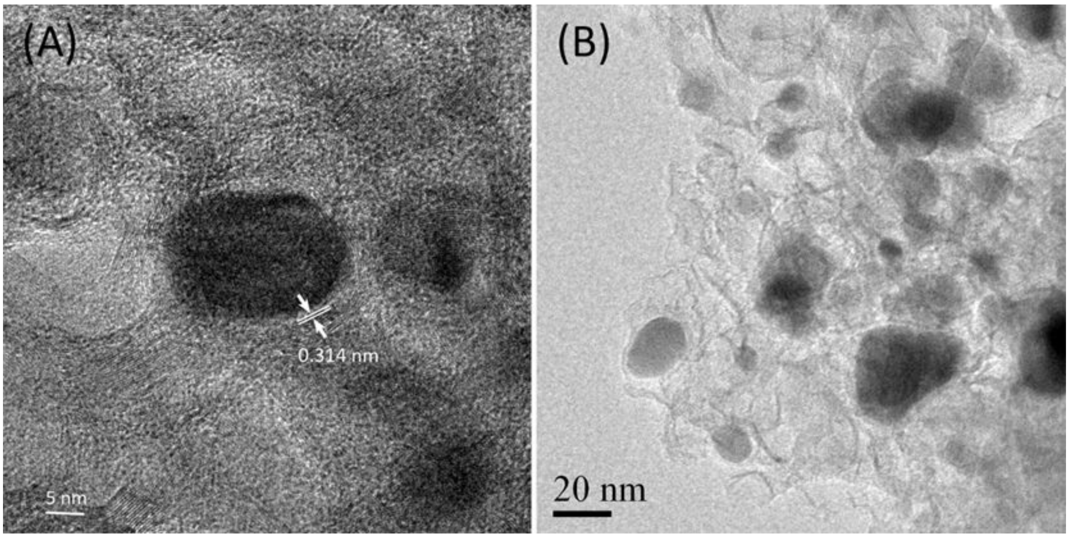

Figure S1 TEM images of pristine (A) and treated FeNC@C samples (B).

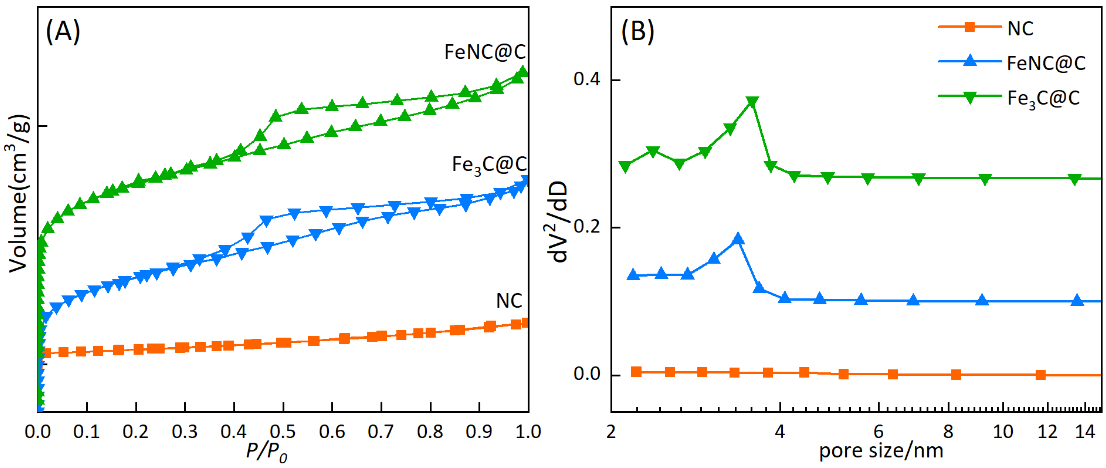

Figure S2 N_2 physical-adsorption isotherms (A) and BJH pore size distribution (B) of samples.

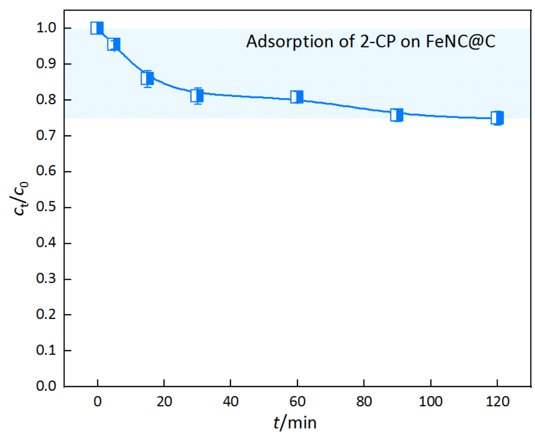

Figure S3 The adsorption kinetic curve of 2-CP on FeNC@C catalyst in solution at pH 3.0 (V=50.0 mL; $c_{catalyst}$=0.5 g/L; [Na_2SO_4]=0.05 M;[2-CP]=0.2 mM; T=298 K).

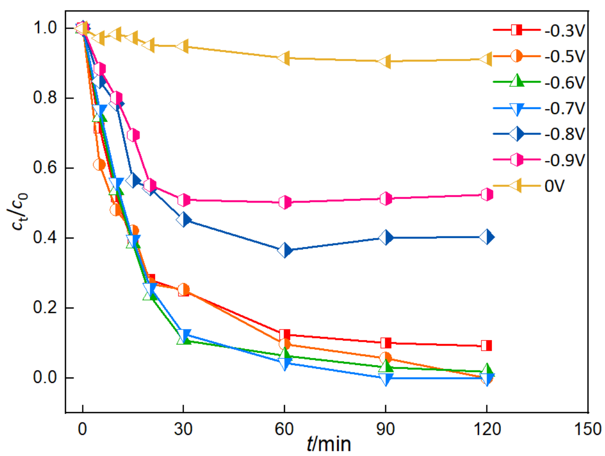

Figure S4 The degradation curves of 2-CP by FeNC@C in HEF system at pH 3.0 with various potentials. (V=50.0 mL; $c_{catalyst}$=0.5 g/L; [Na_2SO_4]=0.05 M;[2-CP]=0.2 mM; O_2 flow rate=0.3 L/min; T=298 K.)

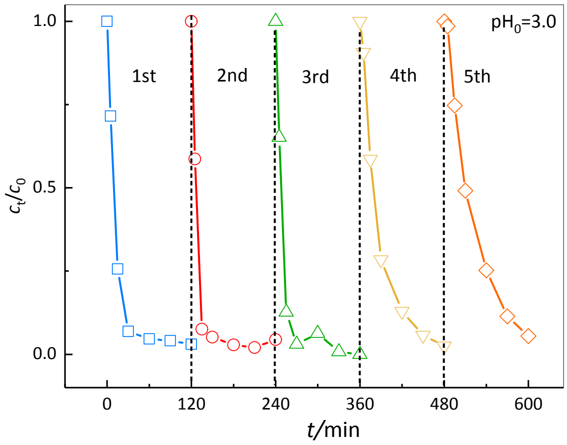

Figure S5 The reusability of FeNC@C in degrading 2-CP in HEF system at pH 3.0. (*V*=50.0 mL; $c_{catalyst}$=0.5 g/L; [Na_2SO_4]=0.05 M;[2-CP]=0.2 mM; O_2 flow rate=0.3 L/min; *T*=298 K)

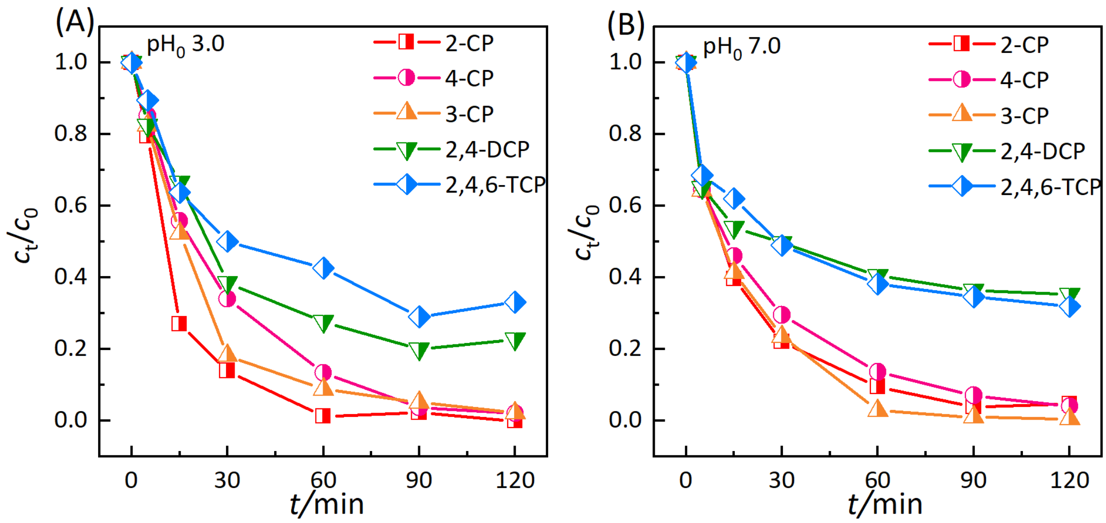

Figure S6 The degradation curves of different chlorophenols by FeNC@C in HEF system at pH 3.0 (A) and 7.0 (B). (*V*=50.0 mL; $c_{catalyst}$=0.5 g/L; [Na_2SO_4]=0.05 M; [chlorophenol]=0.2 mM; O_2 flow rate=0.3 L/min; *T*=298 K)

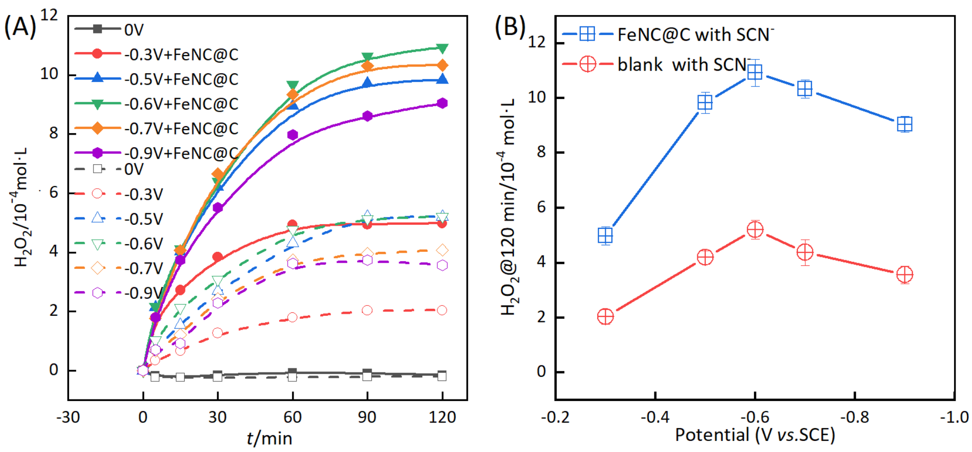

Figure S7 (A) The generation curves of H_2O_2 in FeNC@C heterogeneous EF system in pH 3.0 solution at different potential in the presence of SCN^-. (B) The accumulated H_2O_2 concentration at 120 min in FeNC@C or blank EF system in the presence of SCN^-. (V=50.0 mL; $c_{catalyst}$=0.5 g/L; $[Na_2SO_4]$=0.05 M;$[SCN^-]$=0.2 mM; O_2 flow rate=0.3 L/min; T=298 K; pH_0=3.0)

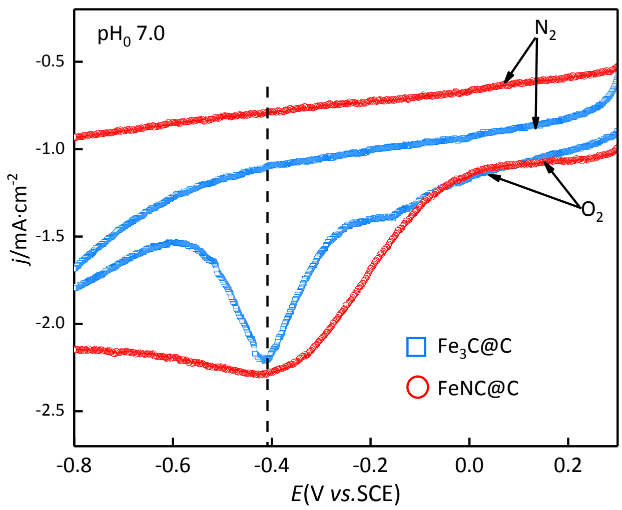

Figure S8 LSV curves of Fe-based catalysts in O_2/N_2 saturated neutral solution. ($[Na_2SO_4]$=0.05 M; pH_0=7.0; T=298K.)

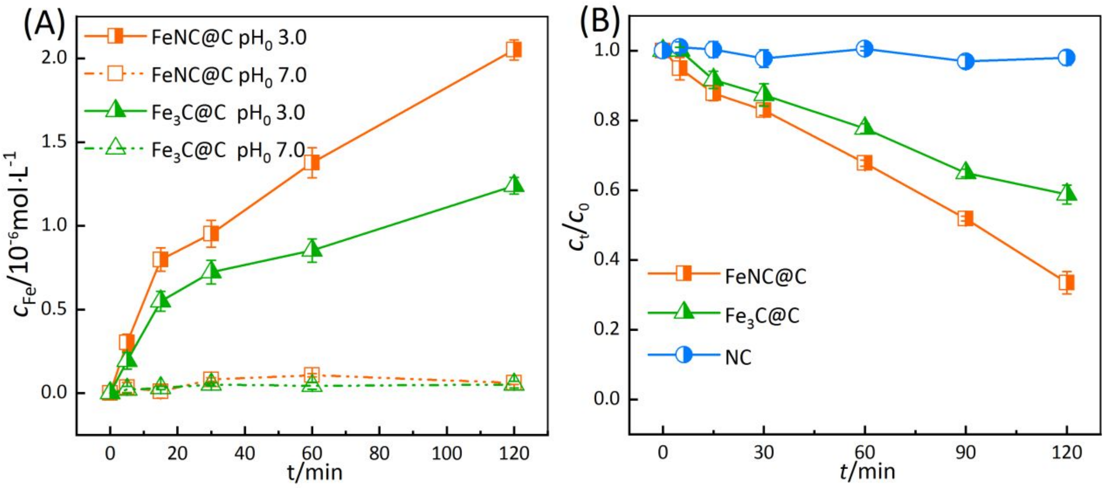

Figure S9 (A) Fe leaching to the aqueous solution under various pH conditions. (B) The decomposition curves of H_2O_2 by Fe-based catalysts in neutral solution. (V=50.0 mL; $c_{catalyst}$=0.5 g/L; T=298 K; [H_2O_2] =10 mM.)

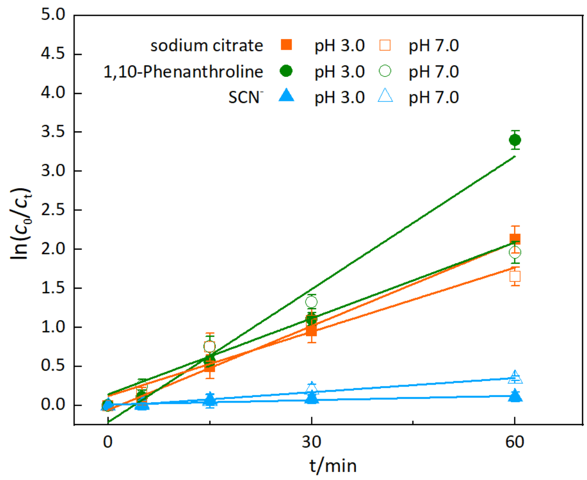

Figure S10 The kinetics fitting curves of 2-CP in Fe-based heterogeneous EF system with poisonous reagents for different Fe species.(V=50.0 mL; $c_{catalyst}$=0.5 g/L; [Na_2SO_4] =0.05 M;[2-CP]=0.2 mM; O_2 flow rate=0.3 L/min; T=298 K;[sodium citrate]=[SCN^-]=[1,10-phenanthroline]=100 mM.)

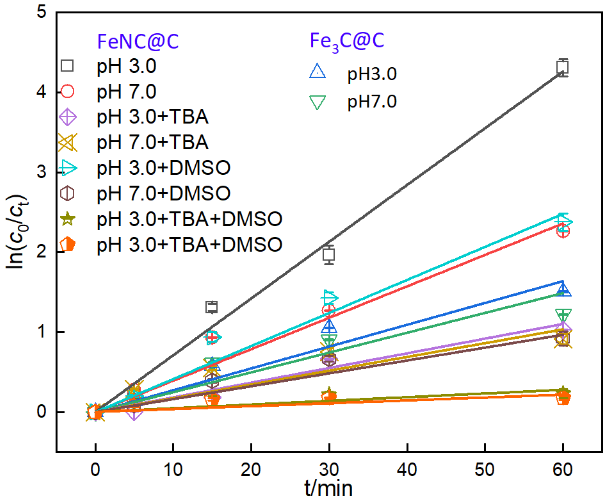

Figure S11 The kinetic curves of 2-CP in Fe-based heterogeneous EF system with different radical scavengers. (*V*=50.0 mL; $c_{catalyst}$=0.5 g/L; [Na_2SO_4] =0.05 M;[2-CP]=0.2 mM; O_2 flow rate=0.3 L/min; *T*=298 K; [DMSO]=[TBA]=100 mM.)

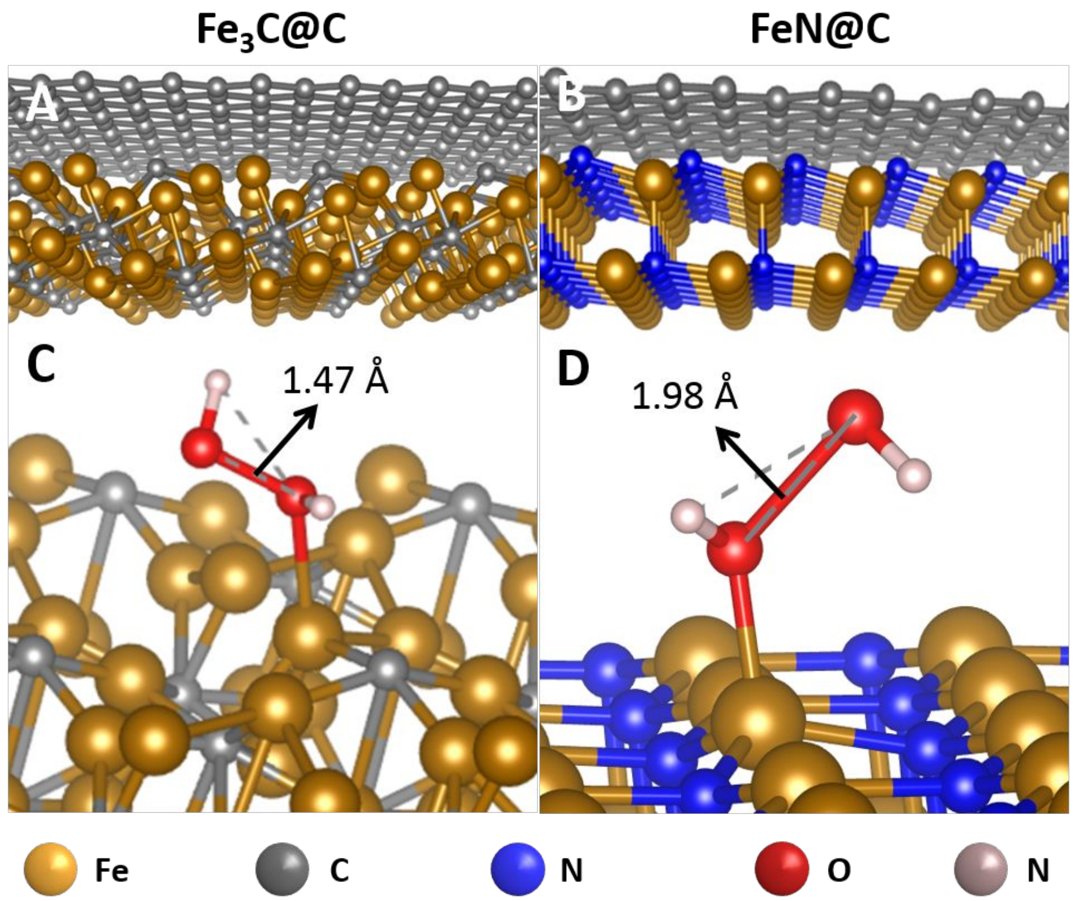

Figure S12 Optimized structures of FeNC@C catalyst. (A) Fe_3C; (B) FeN; (C) H_2O_2 adsorbed on Fe_3C); (D) H_2O_2 adsorbed on FeN.

References

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