Electronic Supplementary Information

Fe/Fe_3C nanoparticles decorated N-doped carbon nanofibers for improving nitrogen selectivity of electrocatalytic nitrate reduction

Yue Lan,[a] Junliang Chen,[a] Hui Zhang,[a] Wei-xian Zhang[b] and Jianping Yang*[a]

[a] State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, College of Materials Science and Engineering, Donghua University, Shanghai 201620, China

[b] College of Environmental Science and Engineering, State Key Laboratory of Pollution Control and Resources Reuse, Tongji University, Shanghai 200092, China.

E-mail for corresponding author: jianpingyang@dhu.edu.cn

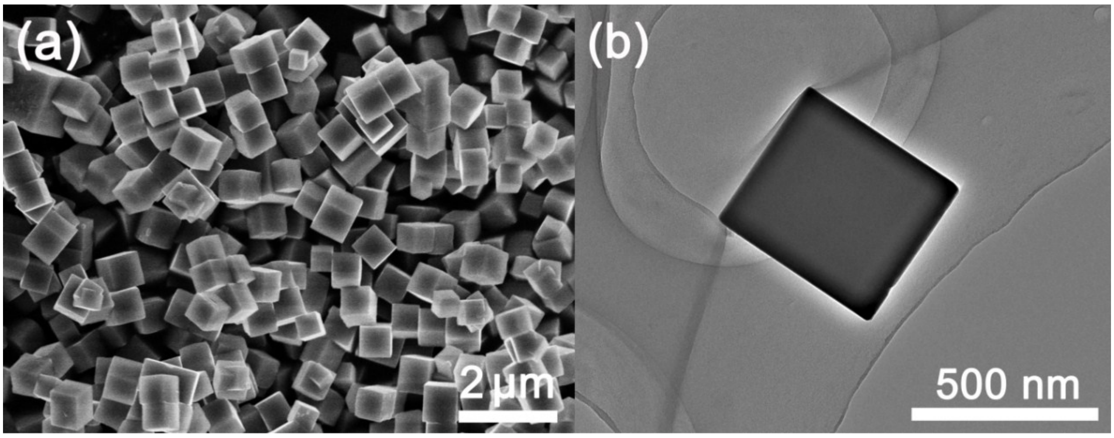

Fig. S1 (a) SEM image, and (b) TEM image of Prussian blue.

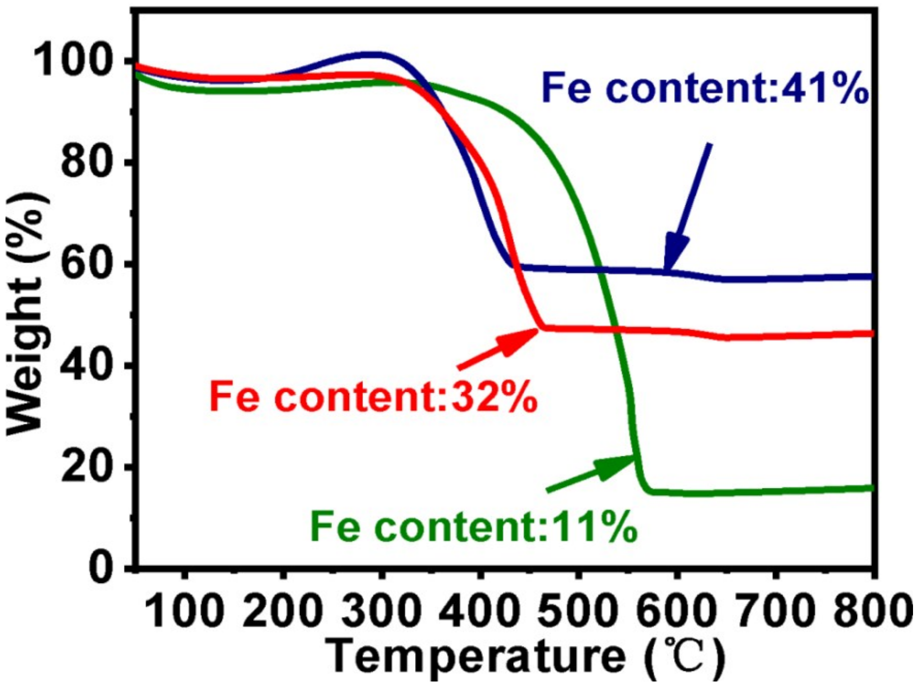

Fig. S2 TGA curves of Fe/Fe_3C-NCNF-1 (iron content: 11%, pyrolysis at 500 °C), Fe/Fe_3C-NCNF-2 (iron content: 32%, pyrolysis at 500 °C), Fe/Fe_3C-NCNF-3 (iron content: 41%, pyrolysis at 500 °C).

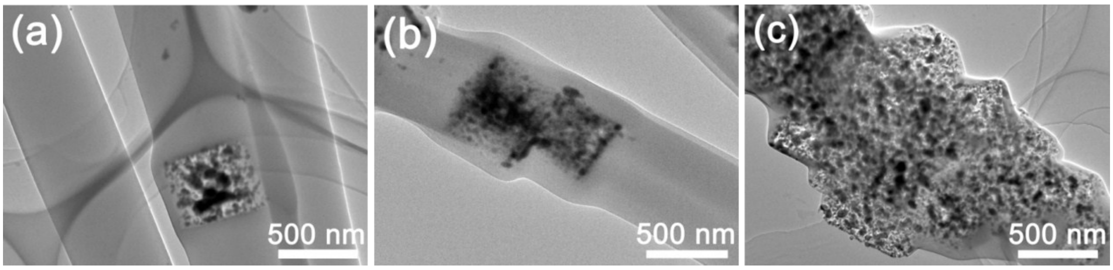

Fig. S3 (a-c) TEM images of Fe/Fe_3C-NCNF-1 (iron content: 11%, pyrolysis at 500 °C), Fe/Fe_3C-NCNF-2 (iron content: 32%, pyrolysis at 500 °C), Fe/Fe_3C-NCNF-3 (iron content: 41%, pyrolysis at 500 °C).

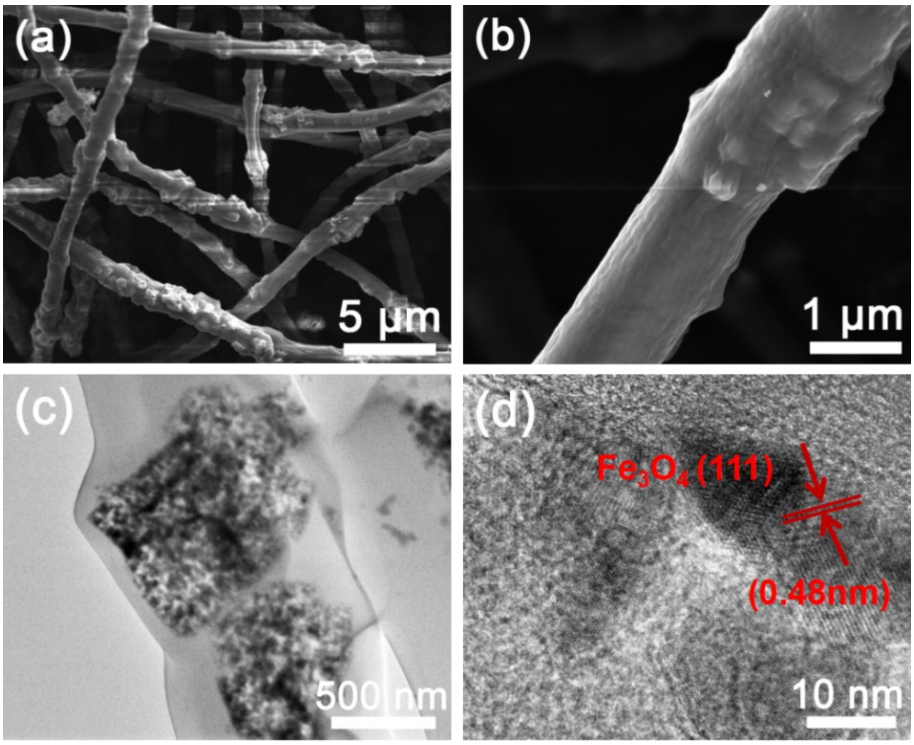

Fig. S4 (a, b) SEM images, (c) TEM image, and (d) HRTEM image of Fe/Fe_3C-NCNF-2-400 (iron content: 32%, pyrolysis at 400 °C).

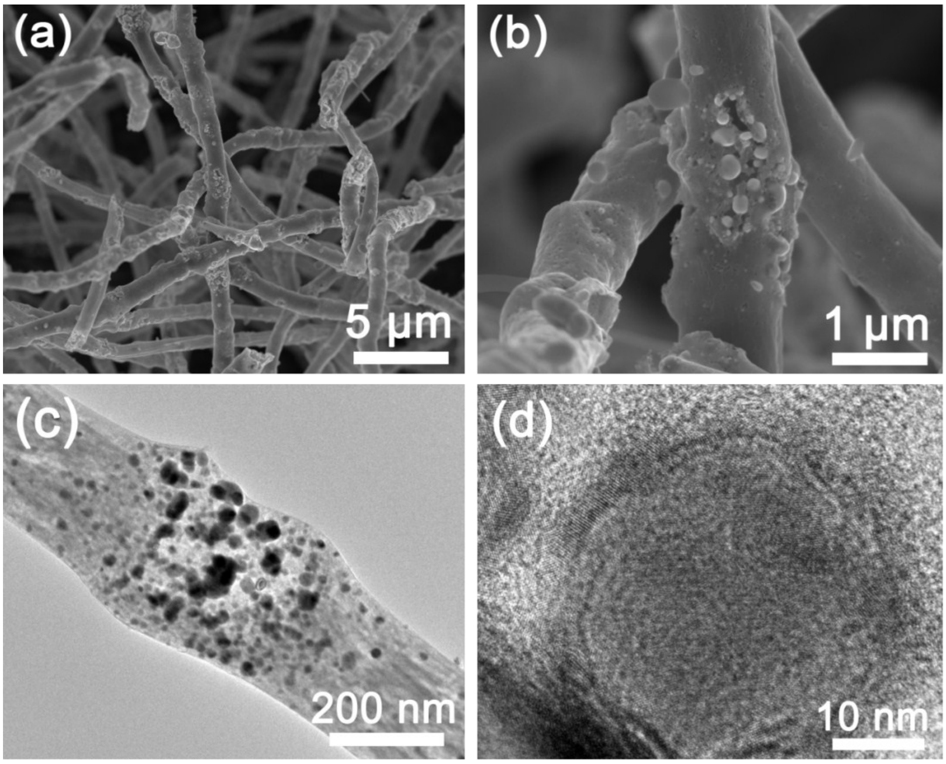

Fig. S5 (a, b) SEM images, (c) TEM image, and (d) HRTEM image of Fe/Fe_3C-NCNF-2-600 (iron content: 32%, pyrolysis at 600 °C).

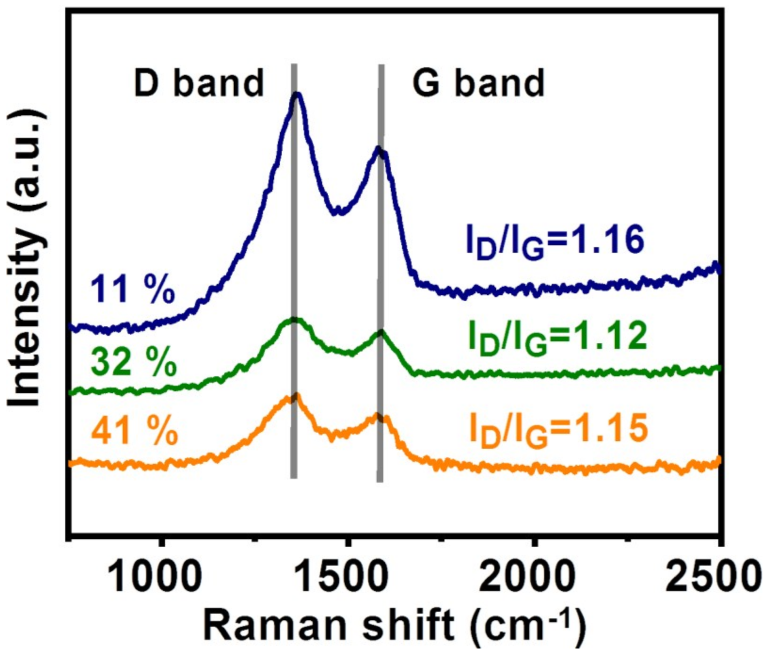

Fig. S6 Raman spectra of Fe/Fe_3C-NCNF-1 (iron content: 11%, pyrolysis at 500 °C), Fe/Fe_3C-NCNF-2 (iron content: 32%, pyrolysis at 500 °C), Fe/Fe_3C-NCNF-3 (iron content: 41%, pyrolysis at 500 °C).

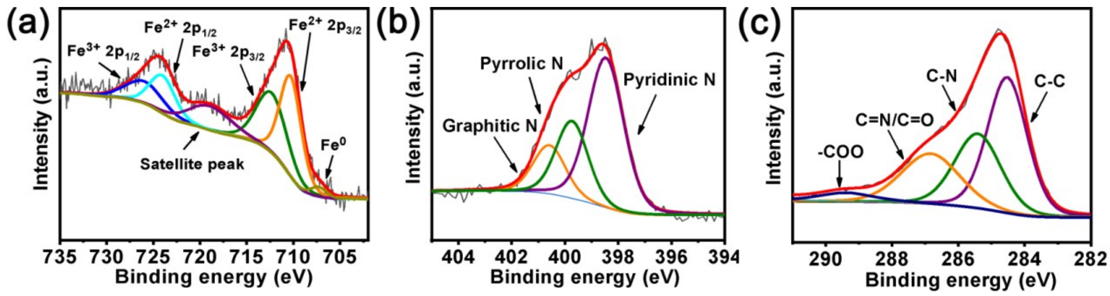

Fig. S7 High resolution XPS spectra of (a) Fe 2p, (b) N 1s, and (c) C 1s of Fe/Fe_3C-NCNF-2-400 (iron content: 32%, pyrolysis at 400 °C).

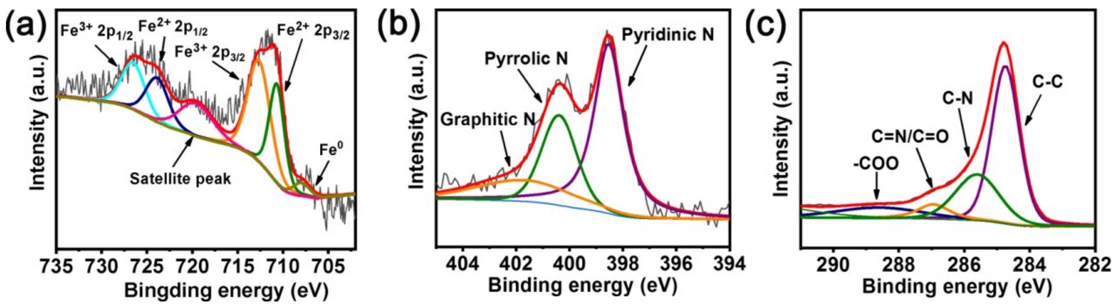

Fig. S8 High resolution XPS spectra of (a) Fe 2p, (b) N 1s, and (c) C 1s of Fe/Fe_3C-NCNF-2-600 (iron content: 32%, pyrolysis at 600 °C).

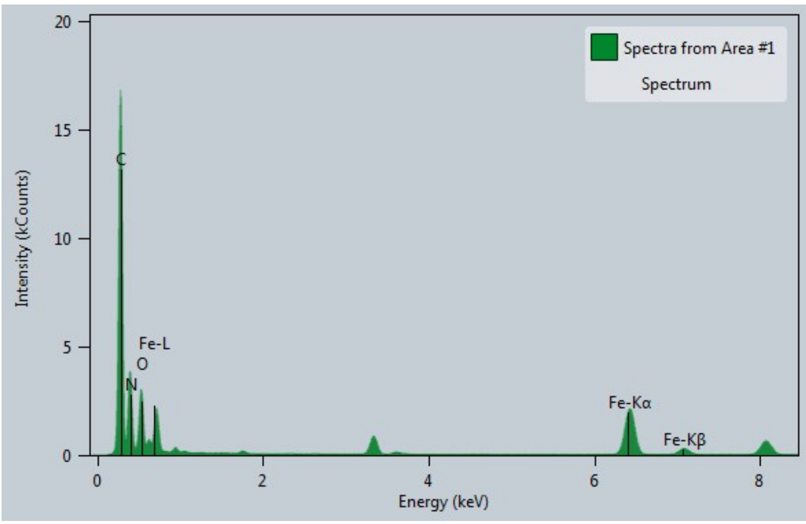

Fig. S9 EDS spectrum of Fe/Fe_3C-NCNF-2 (iron content: 32%, pyrolysis at 500 °C).

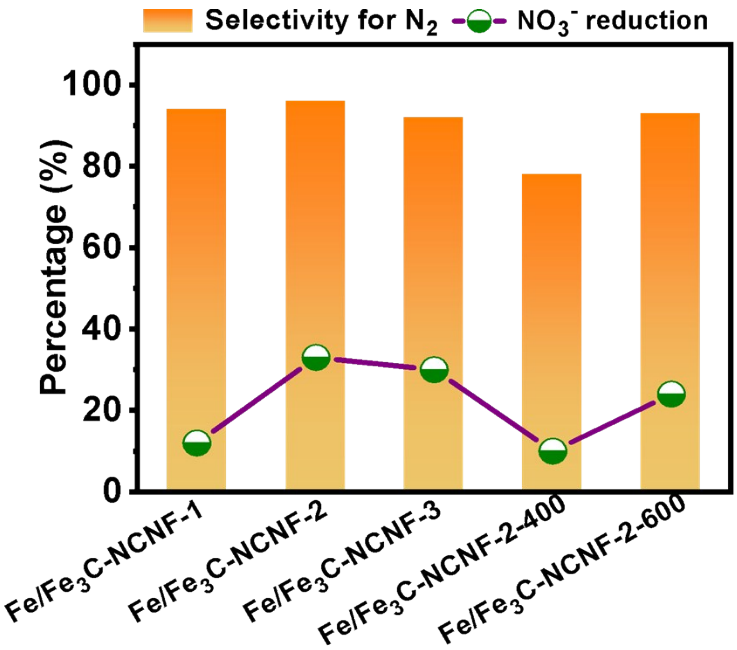

Fig. S10 Conversion percentage of nitrate and nitrogen selectivity of Fe/Fe_3C-NCNF-1 (iron content: 11%, pyrolysis at 500 °C), Fe/Fe_3C-NCNF-2 (iron content: 32%, pyrolysis at 500 °C), Fe/Fe_3C-NCNF-3 (iron content: 41%, pyrolysis at 500 °C), Fe/Fe_3C-NCNF-2-400 (iron content: 32%, pyrolysis at 400 °C), Fe/Fe_3C-NCNF-2-600 (iron content: 32%, pyrolysis at 600 °C). Reaction conditions: initial NO_3^--N concentration 100 mg/L, 0.02 M NaCl at 24 h.

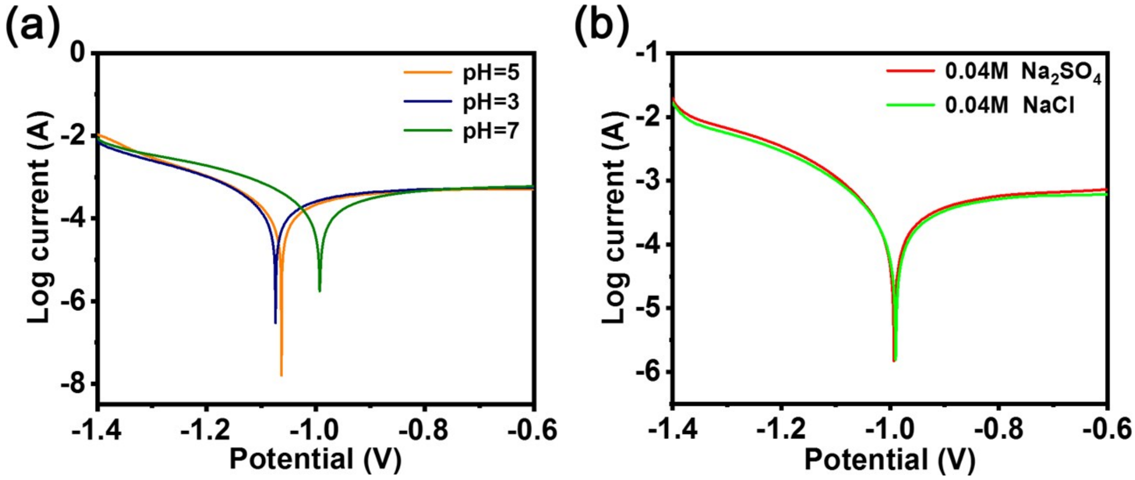

Fig. S11 Potentiodynamic polarization curves of Fe/Fe_3C-NCNF-2 (iron content: 32%, pyrolysis at 500 °C) at (a) different pH values and in (b) 0.04 M Na_2SO_4, 0.04 M NaCl electrolyte. Reaction conditions: initial NO_3^--N concentration 100 mg/L, 0.02 M NaCl for (a), initial NO_3^--N concentration 100 mg/L, 0.04 M NaCl and 0.04 M Na_2SO_4, initial pH value 5 for (b).

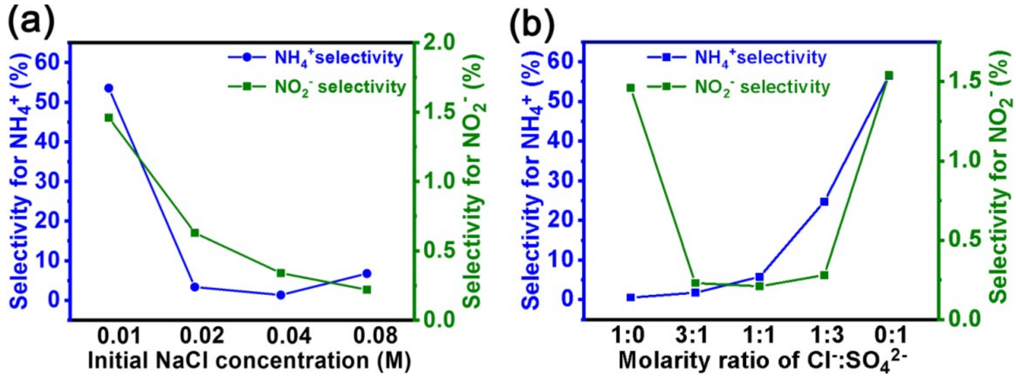

Fig. S12 Effects of (a) initial Cl^- concentration and (b) the molarity ratio of Cl^- and SO_4^{2-} on nitrite selectivity and ammonia selectivity of Fe/Fe_3C-NCNF-2 (iron content: 32%, pyrolysis at 500 °C). Reaction conditions: initial NO_3^--N concentration 100 mg/L, initial pH value 5 at 24 h for (a), initial NO_3^--N concentration 100 mg/L, initial pH value 5 at 24 h for (b).

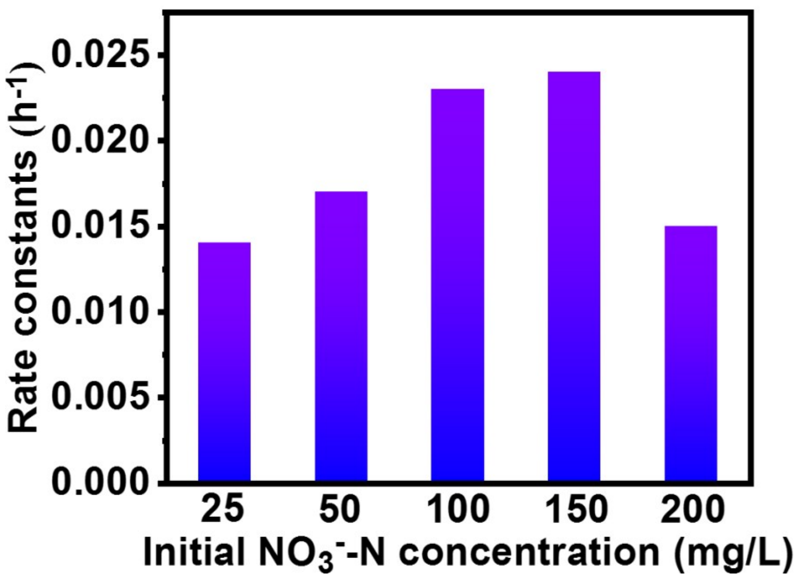

Fig. S13 The rate constants of electrocatalytic denitrification of Fe/Fe_3C-NCNF-2 (iron content: 32%, pyrolysis at 500 °C) at different initial NO_3^--N concentrations. Reaction conditions: initial NO_3^--N concentration 100 mg/L, 0.03 M NaCl and 0.01 M Na_2SO_4 and initial pH value 5 at 24 h.

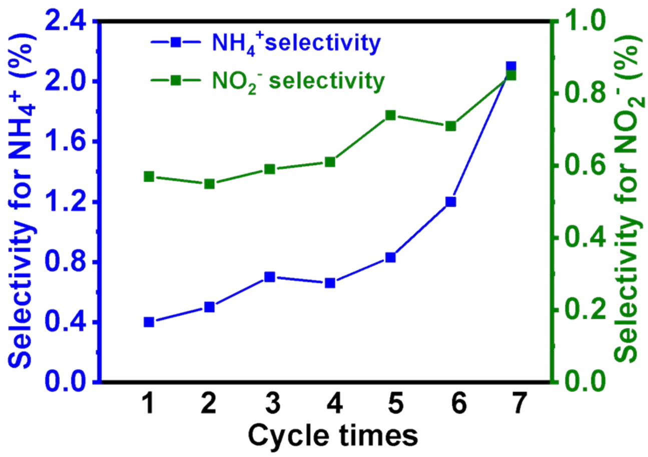

Fig. S14 nitrite selectivity and ammonia selectivity of Fe/Fe_3C-NCNF-2 over 7 cycles test of electrocatalytic denitrification. Reaction conditions: initial NO_3^--N concentration 100 mg/L, 0.03 M NaCl and 0.01 M Na_2SO_4, initial pH value 5 at 24 h.

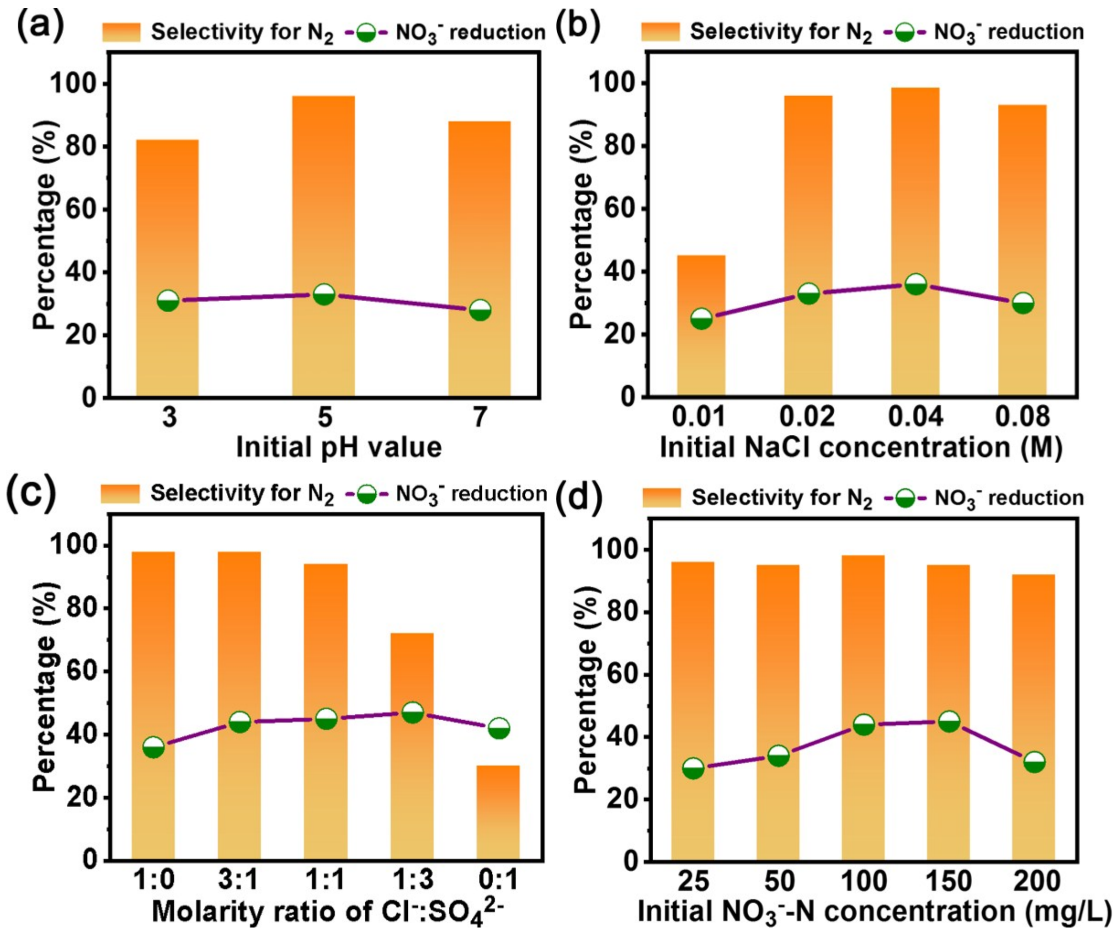

Fig. S15 Effects of (a) initial pH value, (b) initial Cl^- concentration, (c) the molarity ratio of Cl^- and SO_4^{2-}, (d) initial NO_3^--N concentration on conversion percentage of nitrate and nitrogen selectivity of Fe/Fe_3C-NCNF-2 (iron content: 32%, pyrolysis at 500 °C). Reaction conditions: initial NO_3^--N concentration 100 mg/L, 0.02 M NaCl at 24 h for (a), initial NO_3^--N concentration 100 mg/L, initial pH value 5 at 24 h for (b), initial NO_3^--N concentration 100 mg/L, initial pH value 5 at 24 h for (c), initial NO_3^--N concentration 100 mg/L, 0.03 M NaCl and 0.01 M Na_2SO_4 and initial pH value 5 at 24 h for (d).

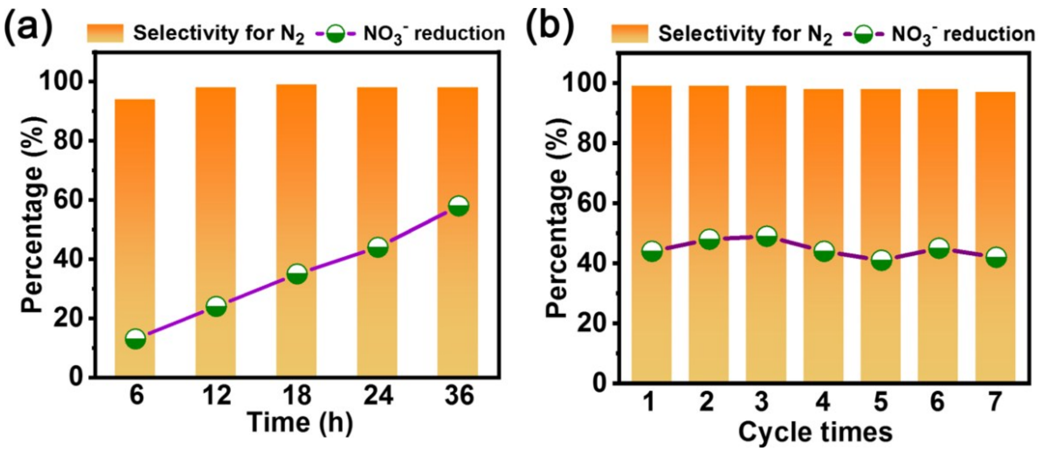

Fig. S16 (a) Conversion percentage of nitrate and nitrogen selectivity of Fe/Fe_3C-NCNF-2 (iron content: 32%, pyrolysis at 500 °C) at different reaction time, (b) conversion percentage of nitrate and nitrogen selectivity over 7 cycles test of electrocatalytic denitrification. Reaction conditions: initial NO_3^--N concentration 100 mg/L, 0.03 M NaCl and 0.01 M Na_2SO_4, initial pH value 5 at 24 h.

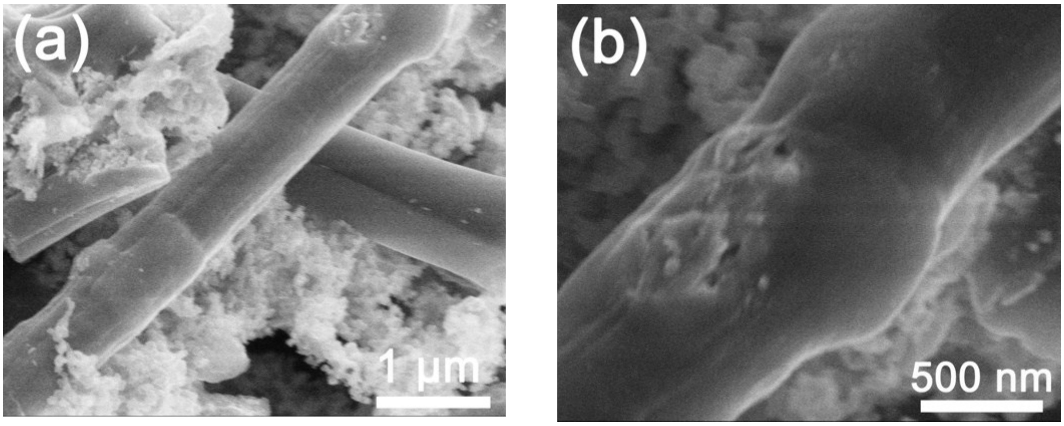

Fig. S17 (a,b) SEM images of Fe/Fe$_3$C-NCNF-2 after 7 cycles test of electrocatalytic denitrification of Fe/Fe$_3$C-NCNF-2 (iron content: 32%, pyrolysis at 500 °C).

Table S1 The content of total nitrogen and different nitrogen species

Catalysts	Calcination Temperature (°C)	Total N (%)	Pyridinic N (%)	Pyrrolic N (%)	Graphitic N (%)
Fe/Fe_3C-NCNF-2-400	400	13.57	7.71	5.59	2.27
Fe/Fe_3C-NCNF-2	500	11.27	6.78	2.89	1.60
Fe/Fe_3C-NCNF-2-600	600	5.00	2.17	1.63	1.20

Table S2 The comparison of electrocatalytic performance of different catalysts for nitrate removal.

Materials	Initial pH	Concentration of electrolyte	Catalysts dosage (mg)	N_2 selectivity (%)	Ref.
nZVI@OMC	/	0.02 M NaCl	4	74	1
Pd_4Cu_4@N-pC	/	0.1 M Na2SO4	4	80	2
Fe@N-C	/	50 mM Na2SO4	60	~100	3
SnPd-NZSM	5.0-6.0	/	250	91	4
Cu/Pd@OMC	/	0.1 M Na2SO4	40	74	5
ZVT	7.2	Cl^- : 12.0 mg/L SO_4^{2-} : 28.0 mg/L Ca^{2+}: 29.4 mg/L Mg^{2+}: 5.3 mg/L	/	78.5	6
nZVI/AC	7.0	/	200	5.5	7
Fe/Fe_3C-NCNF-2	5.0	0.03 M NaCl 0.01 M Na2SO4	4	~100	This work

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