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Supporting Information

Boosting electrocatalysis of nitrate to nitrogen with iron nanoparticles embedded in carbon microspheres

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Fabrication of Fe@C

The iron nanoparticles embedded in carbon spheres were synthesized as follows.[1]Typically, 800 mg of sucrose and 10 mg of Sodium dodecyl sulfate (SDS) are dissolved in 10 mL of deionized water (SDS as an anionic surfactant, effectively strengthens the connection between the iron nanoparticles and the carbon matrix under the electrostatic attraction interaction during the hydrothermal process), sonicating at room temperature for one hour, then add ferric nitrate nonahydrate (add 0.5 mmol, 1 mmol, 1.5 mmol, and 2 mmol, respectively) and stir well. Subsequently, these mixed solutions are subjected to hydrothermal treatment, first reacting at 150 ° C for 3 hours, and then reacting at 160 ° C for 4 hours. After cooling to room temperature, the obtained product is centrifugally washed three times with a mixed solution of deionized water and ethanol and dried. Finally, carbonized at 500 ℃ for 4h under argon-hydrogen atmosphere. The final products are marked Fe@C-X, where X refers to the amount of iron salt added.

Fabrication of carbon spheres

The preparation process is the same as Fe@C, except that no ferric nitrate nonahydrate is added.

Denitrification electrochemical test and UV-vis analysis

The entire electrochemical test process is conducted on a CHI 660D instrument (Shanghai CHI Instruments Co.) with a three-electrode-cell system. A saturated calomel electrode and a platinum electrode (10 mm × 10 mm) are used as the reference and counter electrodes, respectively. UV-vis spectroscopy (Evolution TM 200, Thermo

Fischer Scientific, USA) is operated to determine the content of nitrate (NO_3^--N), nitrite (NO_2^- -N) and ammonia (NH_4^+-N) in the solution before and after the reaction.

Modified nickel foam (10mmx10mm) is used as the working electrode. Briefly, 4 mg of sample powder, 0.5 mg of acetylene black and 0.05 mL of PVDF (10 g L^{-1}) are grinded together into an ink form, which is evenly coated on the foamed nickel at 70 ° C vacuum drying overnight.

The concentration of NO_3^--N, NO_2^--N and NH_4^+ -N in the solution after catalysis are detected by UV-Vis spectrophotometer. The intermediate product, nitrous oxide, would eventually react with excess hydrogen to produce nitrogen, which was negligible. The final calculation of nitrate (NO_3^--N) removal rate (NR%) and N_2 selectivity(S%) and the removal capacity (RC) were calculated according to the following equation:[2]

$$NR\% = \frac{C_0 - C_t}{C_0} \times 100\%$$

$$S\% = \frac{C_0 - C_1 - C_2 - C_t}{C_0 - C_t} \times 100\%$$

$$RC = \frac{(C_0 - C_t)V}{m}$$

Where C_0 (mg L^{-1}) and C_t mg L^{-1}) were the nitrate(NO_3^--N) concentration at initial time(0 h) and final time(t h), respectively, and C_1 (mg L^{-1}) and C_2 (mg L^{-1}) represent the concentration of nitrite(NO_2^--N) and ammonia(NH_4^+ -N) at the final reaction time(t h), respectively. V was the volume of nitrate solution and m meant the mass of iron.

Characterization

Field-emission scanning electron microscopy (FE-SEM) are taken by Hitachi S4800 (Japan) field-emission scanning electron microscope. Transmission electron

microscopy (TEM) are conducted on a JEM-2100 F microscope (JEOL, Japan) operated at 200 kV. X-ray diffraction (XRD) patterns are carried out a Rigaku D/Max-2550 PC diffractometer (Tokyo, Japan) in the 2θ range of 10° to 90°. The surface chemical composition and atom distribution are analyzed by X-ray photoelectron spectroscopy (XPS). The leaching of iron in the final solution is monitored by Inductive coupled plasma-atomic emission spectrometer (ICP-AES). The iron content of the samples is determined by the TGA Q500 apparatus under air atmosphere in the temperature range of 30 °C–900 °C with a heating rate of 10 °C min^{-1}. Raman spectra is operated on a He-Nelaser with an excitation wavelength of 632.8 nm of a Dilor LabRam-1B microscopic Raman spectrometer (France). The Brunauer-Emmett-Teller (BET) method and Barrett-Joyner-Halenda (BJH) model are performed to calculate the specific surface area and pore size distribution.

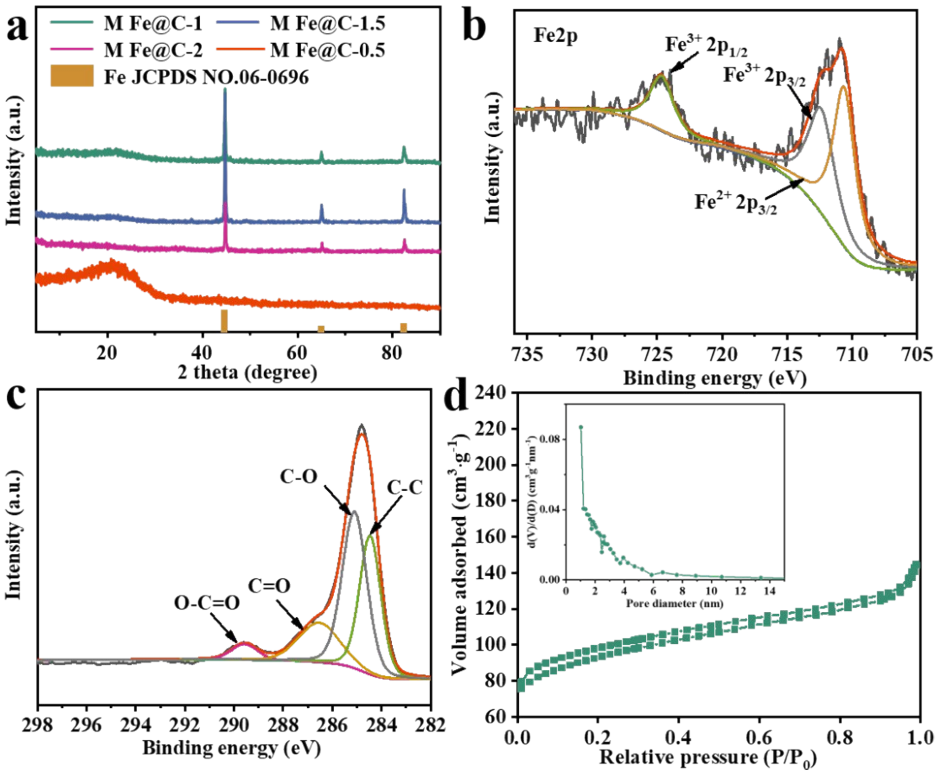

Fig. S1 (a) XRD patterns of Fe@C. (b) Fe 2p X-ray photoelectron spectrum of Fe@C-1. (c) C 1s X-ray photoelectron spectrum of Fe@C-1. (d) N_2 adsorption-desorption isotherms of Fe@C-1 and pore size distribution curves.

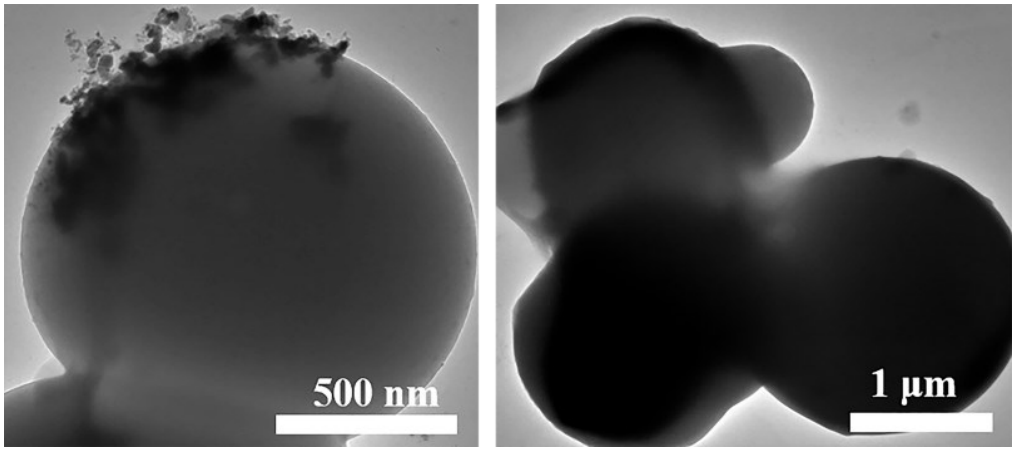

Fig. S2 The TEM images of Fe@C-1.

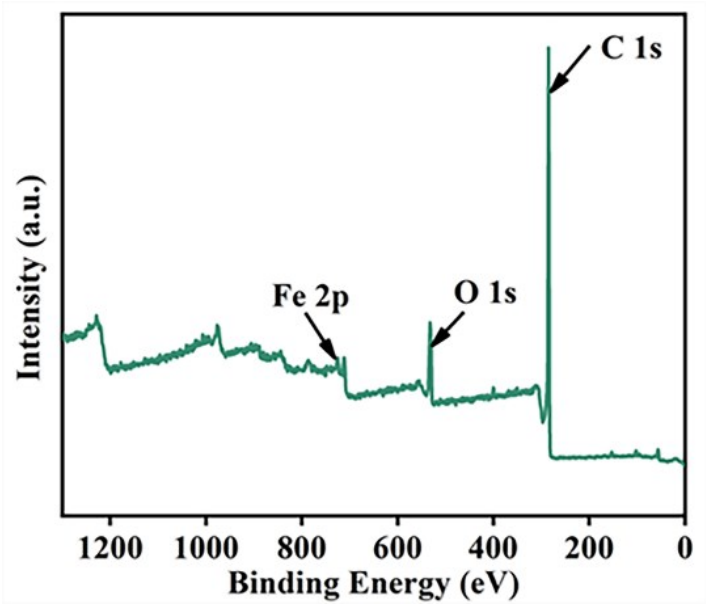

Fig. S3 The XPS spectra of Fe@C-1.

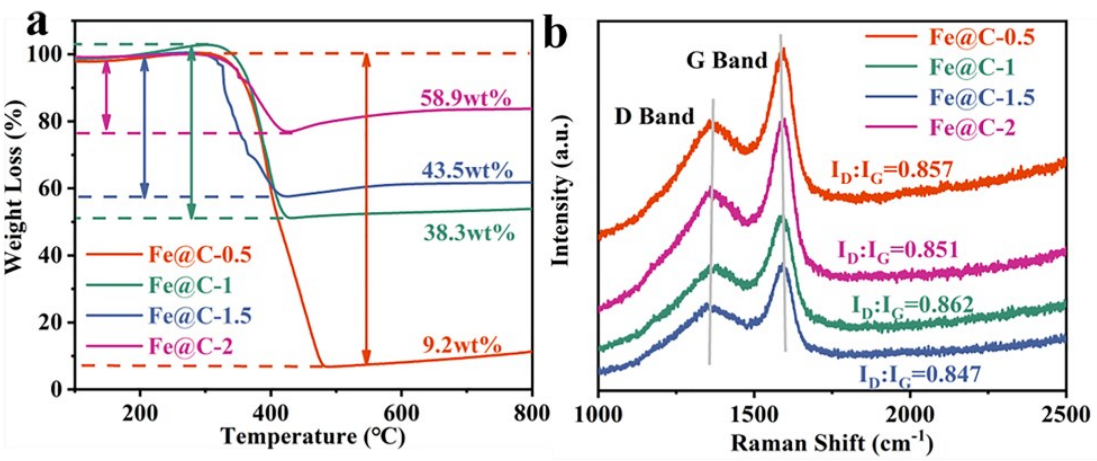

Fig. S4 (a) TGA curves and (b) Raman spectra of Fe@C-X.

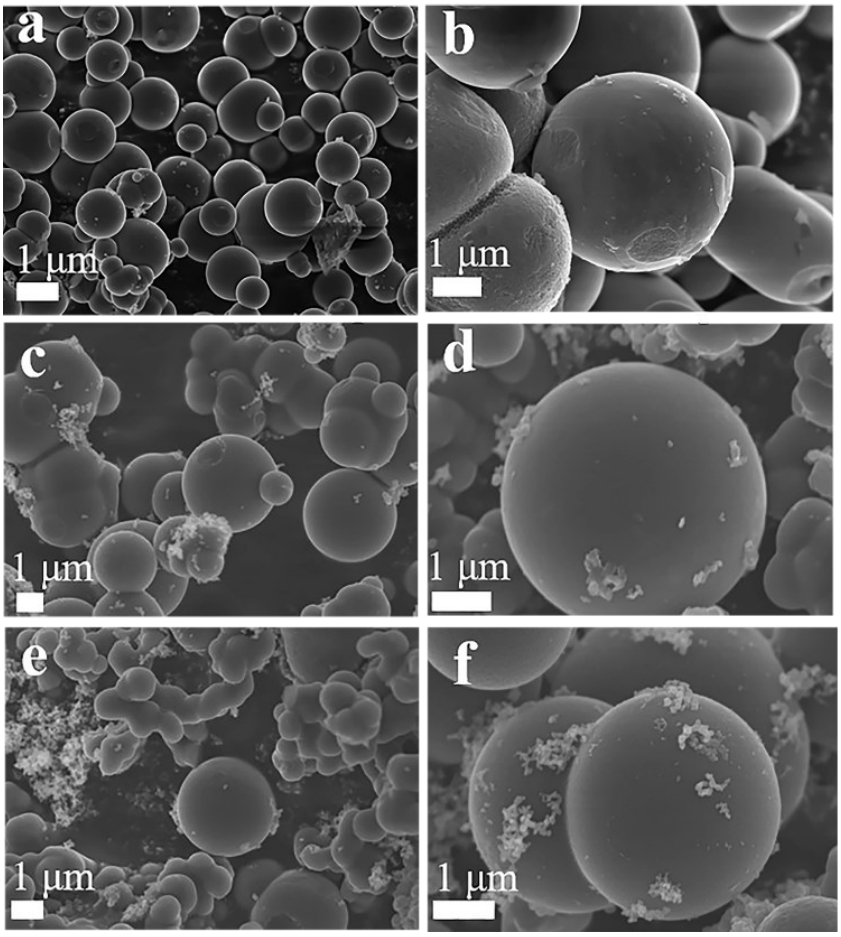

Fig. S5 The SEM images of Fe@C-X, (a，b) Fe@C-0.5, (c，d) Fe@C-1.5, (e，f) Fe@C-2.

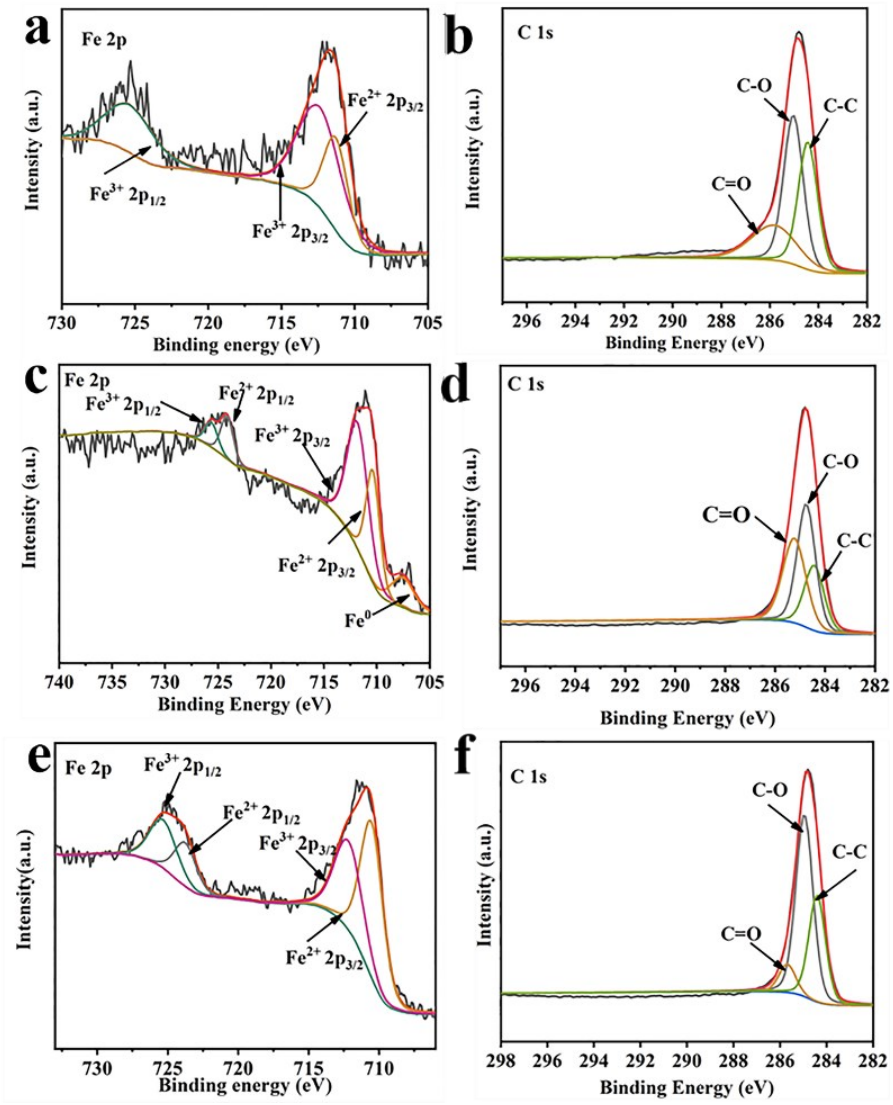

Fig. S6 (a)-(b) Fe 2p X-ray and C 1s X-ray Fe@C-0.5, (c)-(d) Fe 2p X-ray and C 1s X-ray of Fe@C-1.5, respectively. (e)-(f) Fe 2p X-ray and C 1s X-ray of Fe@C-2, respectively.

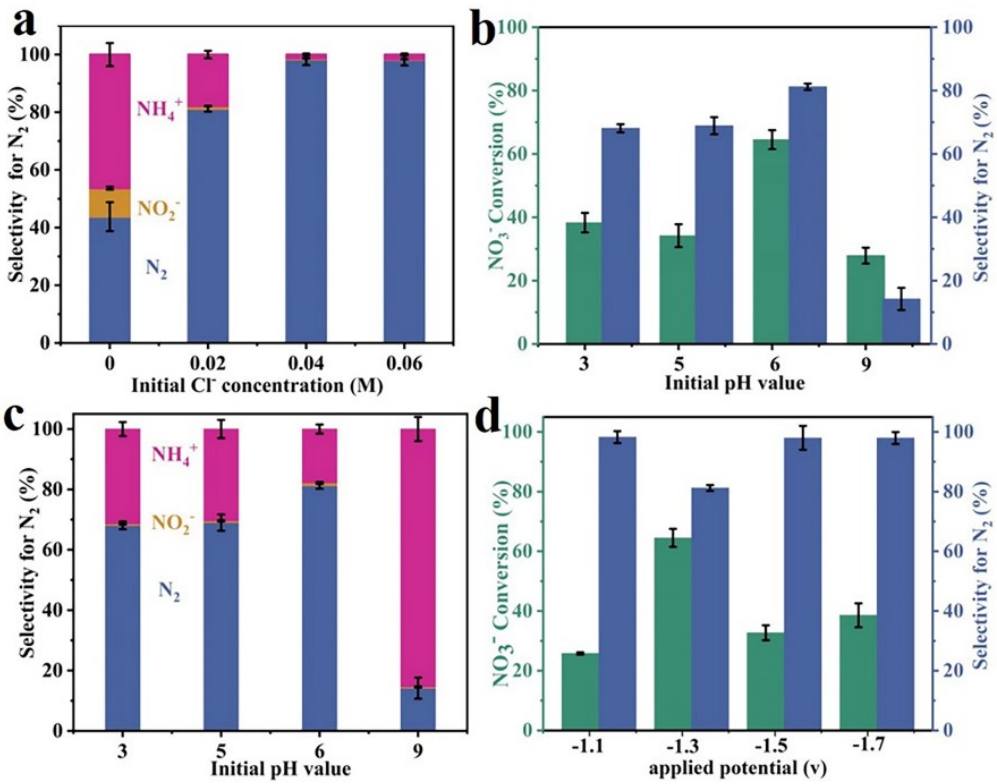

Fig. S7 (a) N_2, NH_4^+, NO_2^- selectivity of Fe@C-1 at different Cl^- concentrations, -1.3V versus SCE, initial NO_3^--N concentration, 100 mg L^{-1} for 24 h. (b) Different pH values, 0.02 M NaCl, initial NO_3^--N concentration, 100 mg L^{-1} for 24 h, -1.3V versus SCE. (c) N_2, NH_4^+, NO_2^- selectivity of different pH values. (d) Different applied potentials, 0.02 M NaCl, initial NO_3^--N concentration, 100 mg L^{-1} for 24 h. (The initial pH of tested water is about 6.1±0.1.)

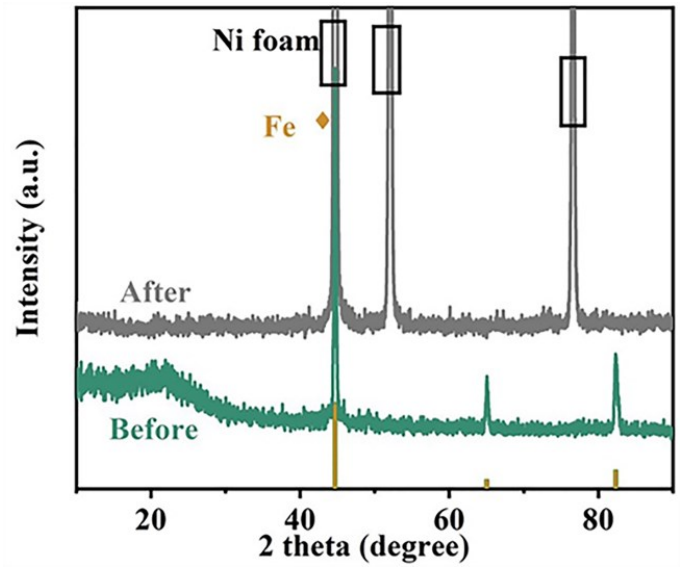

Fig. S8 The XRD pattern of Fe@C-1 after electrocatalytic reaction in 0.02 M NaCl solution with 100 mg L^{-1} nitrate solution for 24h. (The initial pH of tested water is about 6.1±0.1.)

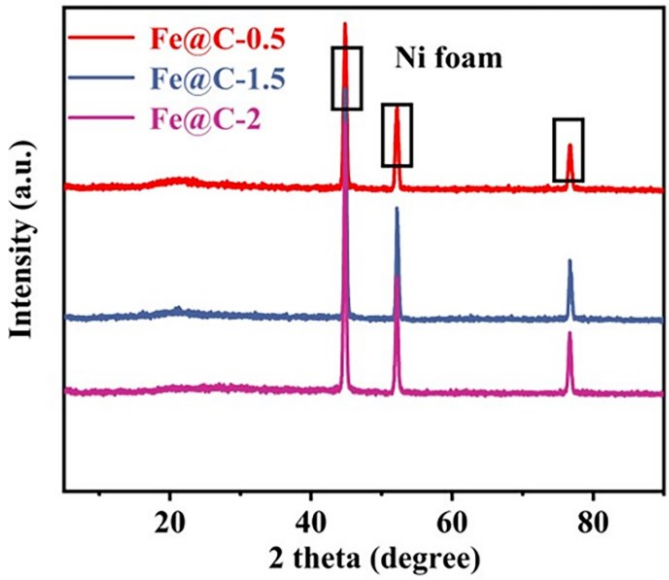

Fig. S9 The XRD pattern of Fe@C-0.5, Fe@C-1.5, Fe@C-2 after electrocatalytic reaction in 0.02 M NaCl solution containing 100 mg L^{-1} nitrate N solution response 24h. (The initial pH of tested water is about 6.1±0.1.)

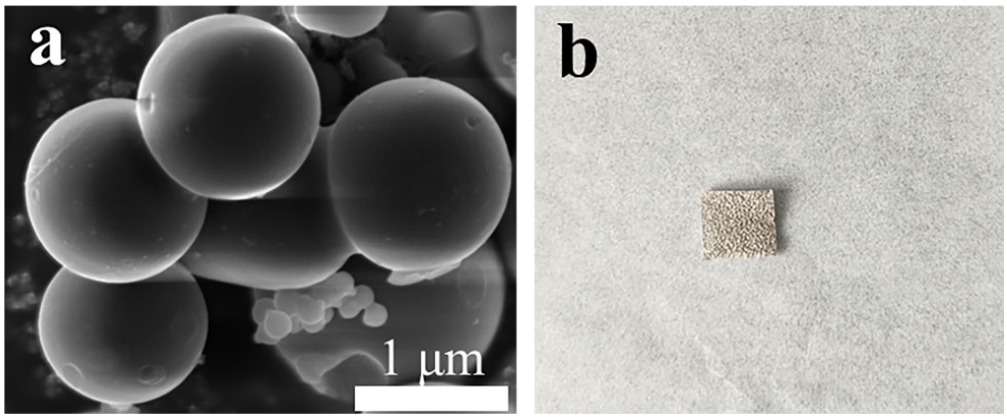

Fig. S10 (a) The SEM image of carbon spheres and (b) Ni-foam.

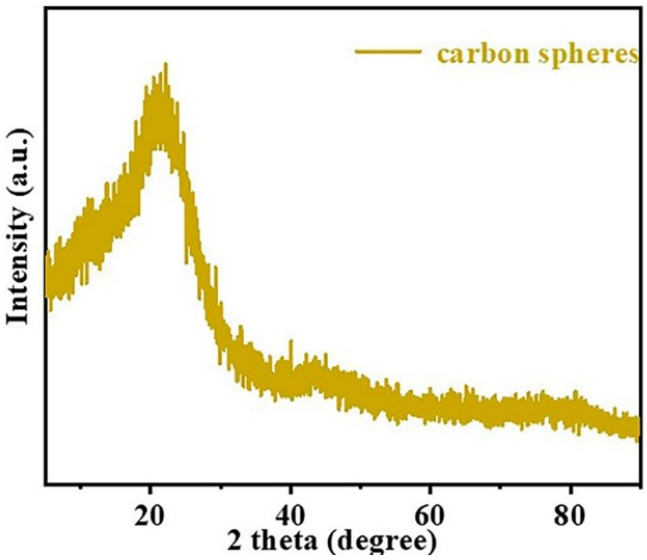

Fig. S11 XRD pattern of carbon spheres.

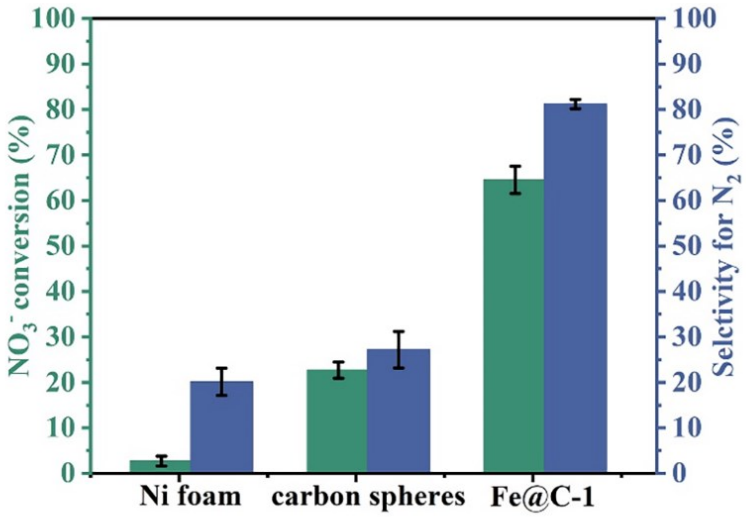

Fig. S12 Nitrate conversion and nitrogen selectivity of Ni foam, carbon spheres and Fe@C-1, initial NO_3^--N concentration, 100 mg L^{-1}, 0.02 M NaCl, for 24h, -1.3V versus SCE. (The initial pH of tested water is about 6.1±0.1.)

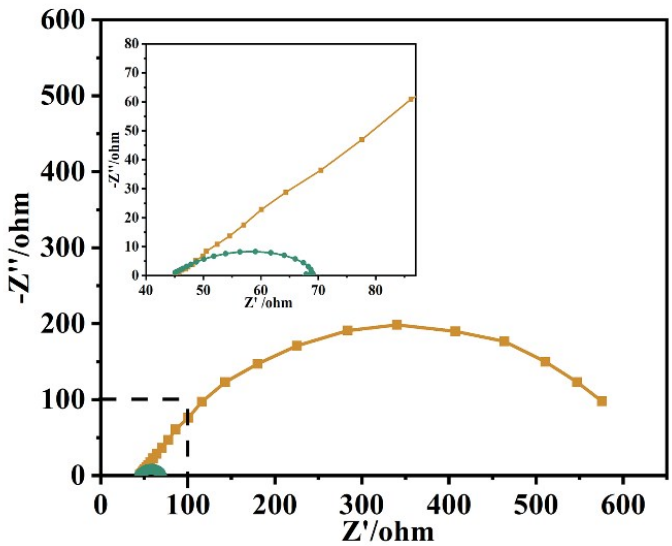

Fig. S13 Nyquist plots for NRR on Fe@C-1 and carbon spheres electrodes at 0.02M NaCl concentration. The brown-yellow line represents the carbon spheres, the green line represents Fe@C-1. v: 5 mV/s, frequency range from 0.01 Hz to 100 kHz.

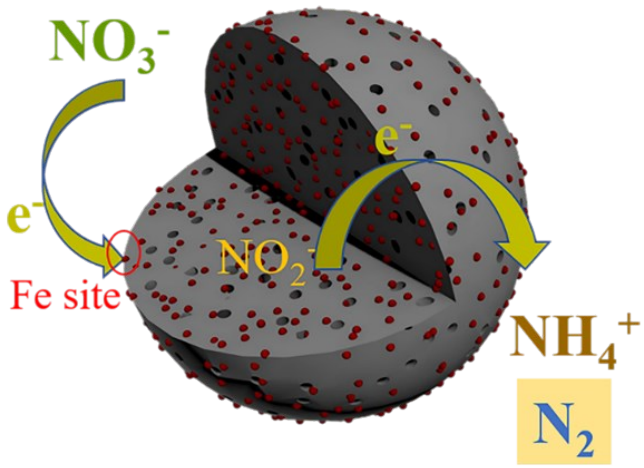

Fig. S14 The electrocatalytic denitrification catalytic mechanism of Fe@C.

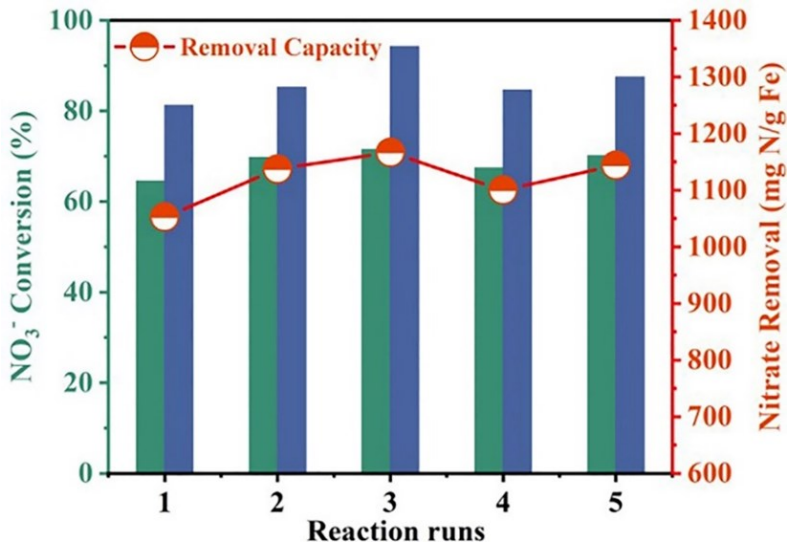

Fig. S15 The stability test for Fe@C-1. Reaction conditions: initial NO_3^--N concentration, 100 mg L^{-1}, 0.02 M NaCl, one cycle is 24 h, -1.3V versus SCE. The dark blue bar graph represents the nitrogen selectivity. (The initial pH of tested water is about 6.1±0.1.)

Table S1 the leaching of iron during the stability test of Fe@C-1.

Reaction runs	1	2	3	4	5
Iron content ($mg\ L^{-1}$)	0.0482	0.3691	0.1354	0.2011	0.0974

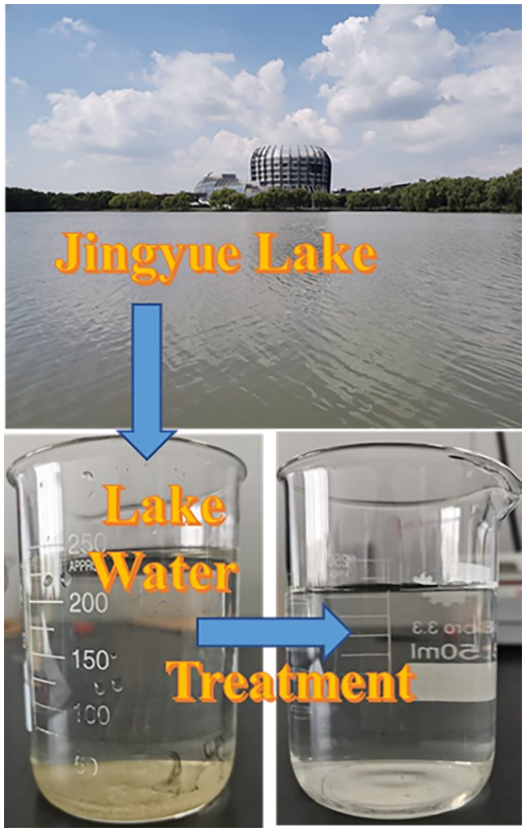

Fig. S16 The real water from Jingyue Lake of Donghua University.

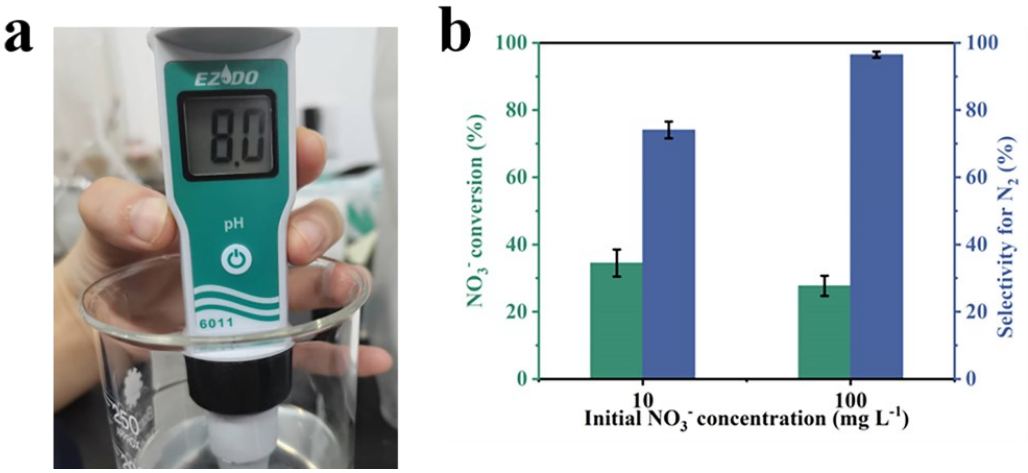

Fig. S17 (a) The initial of Jingyue Lake is pH= 8.0±0.1. (b) Nitrogen selectivity of the real water from Jingyue Lake, -1.3V versus SCE, for 24h.

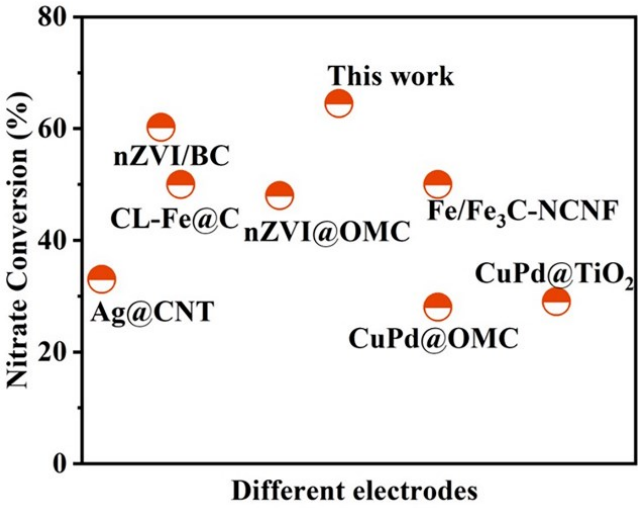

Fig. S18 Comparison of nitrate conversion with different electrodes.

1. H. Sun, G. Zhou, S. Liu, H. M. Ang, M. O. Tade and S. Wang, *ACS Appl. Mater. Interfaces*, 2012, **4**, 6235-6241.

2. M. Chen, H. Wang, Y. Zhao, W. Luo, L. Li, Z. Bian, L. Wang, W. Jiang and J. Yang, *Nanoscale*, 2018, **10**, 19023-19030.