

Supporting Information

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Section A. Supplementary Methods

1. Experimental section

Synthesis of CuFe PBA

The CuFe PBA nanocubes were prepared as previous method with simple modifications. Typically, 6 mmol of cupric acetate monohydrate and 6 mmol of trisodium citrate dihydrate were dissolved in 200 ml of deionized water by sonication for 30 min to obtain solution A. 9 mmol of $K_3Fe(CN)_6$ was added into another 200 ml of deionized water to form solution B. Then, solution B was quickly poured into solution A under vigorous stirring, which was continued for 15 min until a uniformly mixed solution was obtained. The mixed solution was aged at 70 °C for 24 h followed by centrifugation with ethanol and water several times to collect red precipitates. After that, the products of CuFe PBA nanocubes were dried at 60 °C for 12 h.

Synthesis of CuFe PBA/PAN

Briefly, 0.2 g of CuFe PBA nanocubes and 0.36 g of PAN were dispersed to 2.6 ml of DMF solvent, which was vigorously stirred in an oil bath at 60 °C for 24 h to obtain homogeneously dispersed solution. Then, the mixture was injected into 5ml syringe connected with stainless steel. A voltage of 14 kV was applied to the needle; the flow rate of the polymer was set at 0.8 ml/h, and the distance between the needle and the receiver was about 15 cm. The collected fibers were dried in an oven at 70 °C for subsequent carbonization treatment. For comparison, the synthesis of $FeCl_3/PAN$,

Cu(Ac)₂/PAN were synthesized used the same preparation method expect for replacing 0.2 g CuFe PBA with 0.65 mmol iron salt and 1 mmol copper salt, respectively. In addition, PAN was prepared without adding CuFe PBA.

Synthesis of Cu/Fe@NCNFs-T (T represents the temperature)

The obtained CuFe PBA/PAN nanofiber was stabilized in muffle furnace at 260 °C for 2 h with a heating rate of 5 °C/min. The pre-oxidized fiber was calcined in an H₂ atmosphere at 700 °C for 2 h, and the heating rate was controlled at 5 °C/min, which was named Cu/Fe@NCNFs-700. The fibers calcined at 500 °C, 600 °C, and 800 °C under the same conditions are named Cu/Fe@NCNFs-500, Cu/Fe@NCNFs-600, Cu/Fe@NCNFs-800. For comparison, the synthesis of Fe/NCNFs-700, Cu/NCNFs-700, NCNF-700 Cu/Fe-700 used the same preparation method expect for replacing CuFe PBA/PAN with FeCl₃/PAN, Cu(Ac)₂/PAN, PAN and CuFe PBA, respectively.

Characterization

Field emission scanning electron microscope (FE-SEM, Hitachi S4800, Japan) and field emission transmission electron microscope (TEM, JEOL, Japan) are mainly used to analyze and observe the internal microstructure of materials. X-ray diffraction (XRD, Rigaku D/Max-2550 PC, Japan) with Cu α radiation in the range 5–90° was used to analyze the crystalline phase of samples. X-ray photoelectron spectroscopy was used to analyze the elements valence conducting on ESCALAB 250Xi system. Thermogravimetric analysis (TG) was operated on Q5000IR TG-DTA in an air atmosphere in the range of room temperature to 800 °C. The physical properties of carbon materials was analyzed by Raman spectroscopy. Inductively coupled plasma-

atomic emission spectrometer (ICP) was used to measure the metal ion content in the solution.

Electrochemical measurements

All the electrochemical tests were performed using the given 1.3 V constant potential test mode on CHI 660E (Shanghai CHI Instruments Co.) electrochemical workstation, equipped with a three-electrode system. For working electrode, 4 mg prepared Cu/Fe@NCNFs-700, 0.5 mg conductive carbon black were dissolved in 50 ul PVDF with NMP as the solvent to form a uniformly dispersed catalyst ink after fully grinding in a mortar. Then, the catalyst ink was carefully dropped on the 1 cm*1 cm nickel foam and was dried in a vacuum oven at 70 °C for 12 h as the working electrode to be used. Saturated calomel electrode and platinum electrode were selected as reference electrode and counter electrode respectively. In the practical electrochemical measurements, the slightly acidic simulated sewage system (pH=5) consists of 0.1 M Na₂SO₄, 0.02 M NaCl, and different initial concentrations of NaNO₃, in which Na₂SO₄ make contribute to increase the removal capacity of nitrate and Na₂SO₄ was conducive to improving nitrogen selectivity. Cyclic voltammetry (CV) with a sweep rate of 50 mV s⁻¹ was applied to the working electrode to activate the catalyst before the amperometric curve (i-t) test. In addition, different test conditions including given voltage and electrolyte concentration were also used to evaluate the electrocatalytic denitrification activity of Cu/Fe@NCNFs-700.

Analytical methods

At a certain time interval, a specific amount of the reaction solution was extracted to determine the concentration of nitrate, nitrite and ammonia by UV-Vis spectrophotometer. The final product of nitrate reduction was mainly existed in two forms of ammonia or nitrogen and the nitrogen is the desired product owing to its environmentally friendly. The concentration of the nitrate, nitrite and ammonia were calculated according to the standard curve equation based on the absorbance value detected at the specific wavelength 220 nm, 540 nm and 420 nm. A series of data that can be used to analyze the performance of electrocatalytic denitrification, such as the removal capacity of nitrate ($R_{NO_3^-}$ (mg N/g Cu/Fe)), the conversion percentage of nitrate ($C_{NO_3^-}$ (%)), the selectivity of nitrite ($S_{NO_2^-}$ (%)), ammonia ($S_{NH_4^+}$ (%)) and nitrogen (S_{N_2} (%)) were calculated according to the following equations.

$$C_{NO_3^-}(\%) = \frac{C_t(NO_3^-) - C_0(NO_3^-)}{C_0(NO_3^-)} \times 100\%$$

$$R_{NO_3^-}(\text{mg N/g Cu/Fe}) = \frac{[C_0(NO_3^-) - C_t(NO_3^-)] \times V}{m_{Cu/Fe}}$$

$$S_{NO_2^-}(\%) = \frac{C_t(NO_2^-)}{C_0(NO_3^-) - C_t(NO_3^-)} \times 100\%$$

$$S_{NH_4^+}(\%) = \frac{C_t(NH_4^+)}{C_0(NO_3^-) - C_t(NO_3^-)} \times 100\%$$

$$S_{N_2}(\%) = \frac{C_0(NO_3^-) - C_t(NO_3^-) - C_t(NO_2^-) - C_t(NH_4^+)}{C_0(NO_3^-) - C_t(NO_3^-)} \times 100\%$$

Section B. Supplementary Data

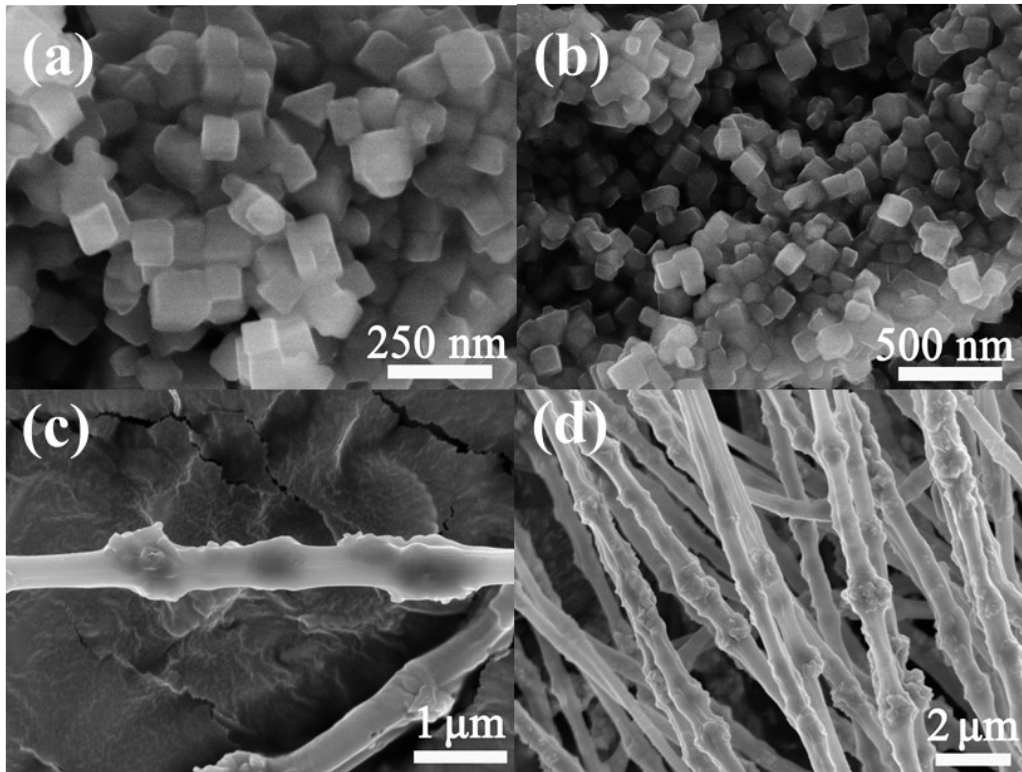


Figure S1. SEM images of (a-b) CuFe PBA, (c-d) CuFe PBA/PAN.

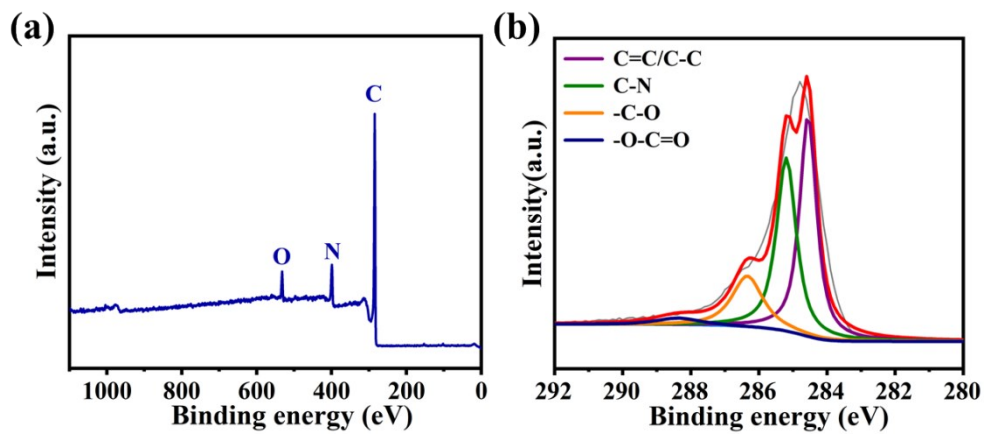


Figure S2. (a) XPS survey spectra, (b) high-resolution C 1s of NCNFs-700.

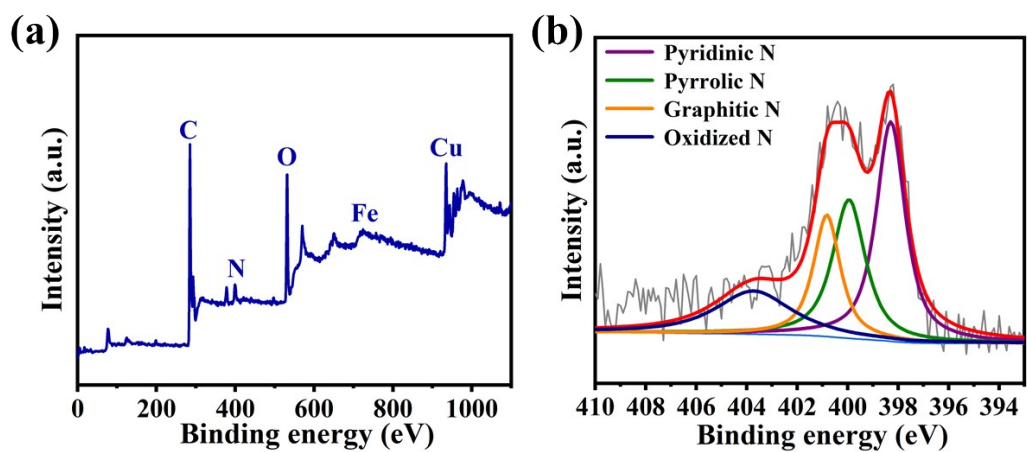


Figure S3. (a) XPS survey spectra, (b) high-resolution N 1s of Cu/Fe@NCNFs-700.

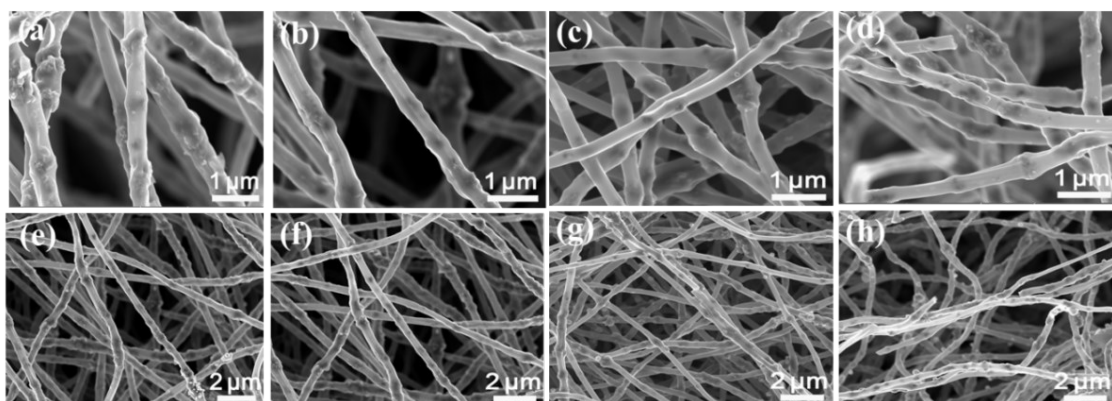


Figure S4. SEM images of (a,e) Cu/Fe@NCNFs-500, (b,f) Cu/Fe@NCNFs-600, (c,g) Cu/Fe@NCNFs-700, (d,h) Cu/Fe@NCNFs-800.

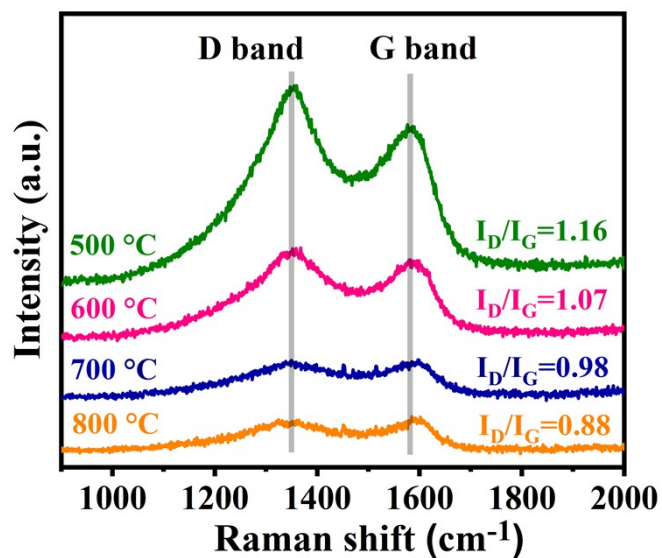


Figure S5. XRD patterns of Cu/Fe@NCNFs-500, Cu/Fe@NCNFs-600, Cu/Fe@NCNFs-700, Cu/Fe@NCNFs-800

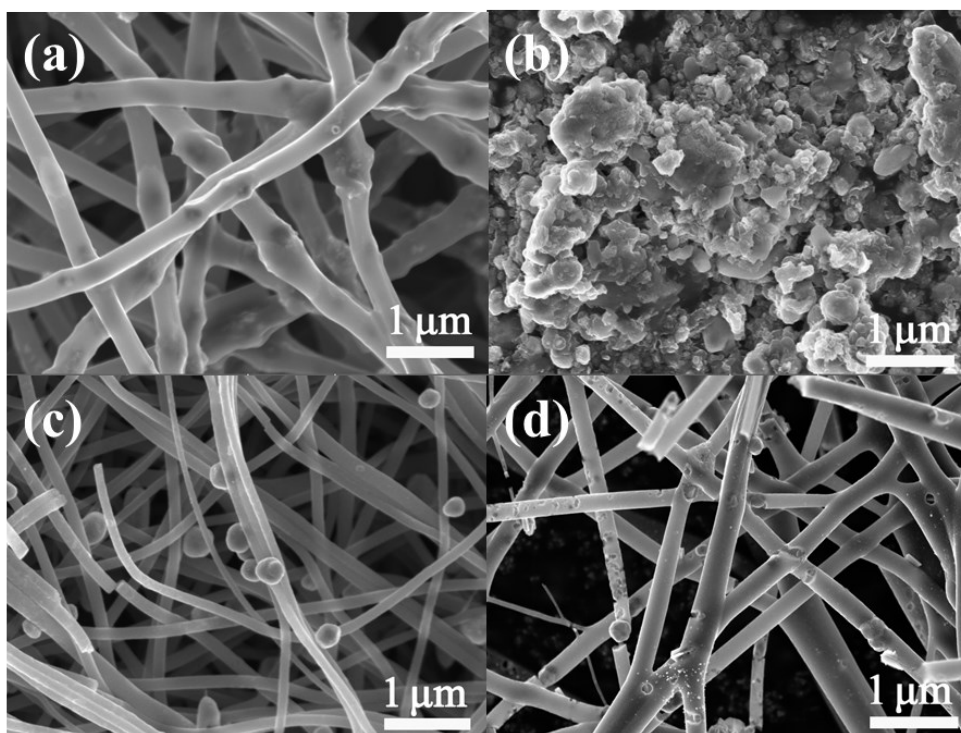


Figure S6. SEM images of (a) Cu/Fe@NCNFs-700, (b) Cu/Fe-700, (c) Cu/NCNFs-700, (d) Fe/NCNFs-700.

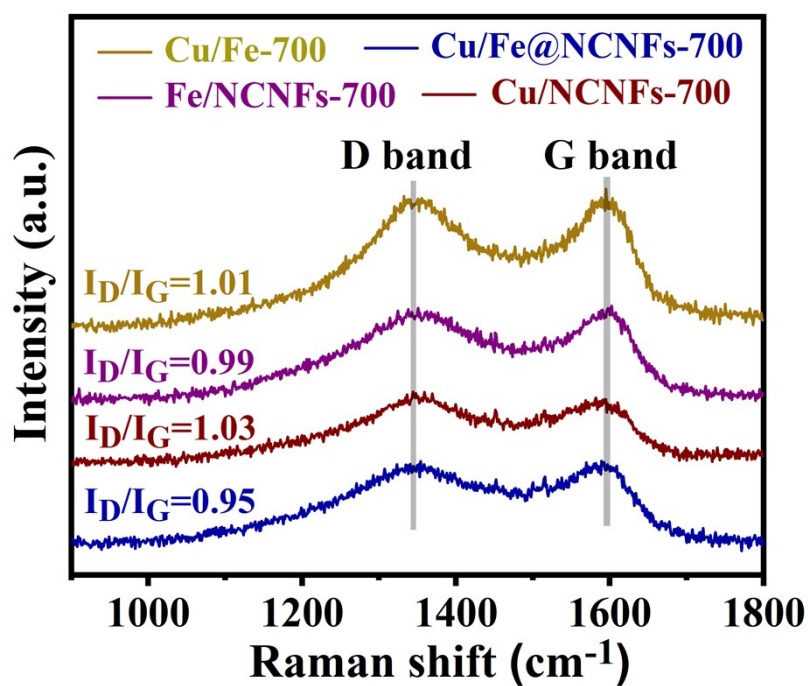


Figure S7. Raman spectra of Cu/Fe-700, Fe/NCNFs-700, Cu/NCNFs-700 and Cu/Fe@NCNFs-700.

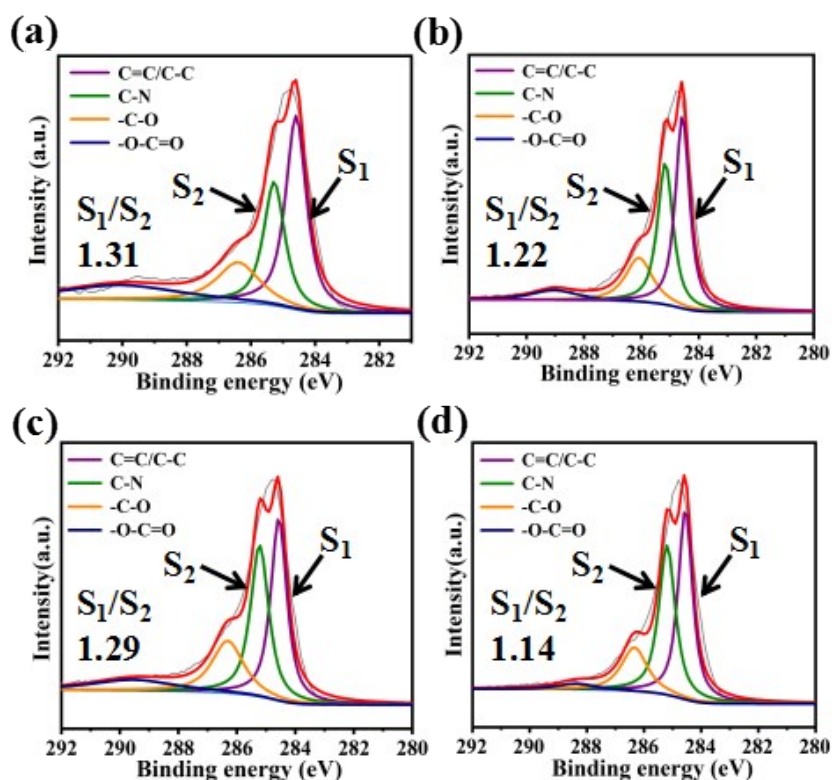


Figure S8. High -resolution C 1s of (a) Cu/Fe@NCNFs-700, (b) Fe/NCNFs-700, (c) Cu/NCNFs-700 and (d) NCNFs-700.

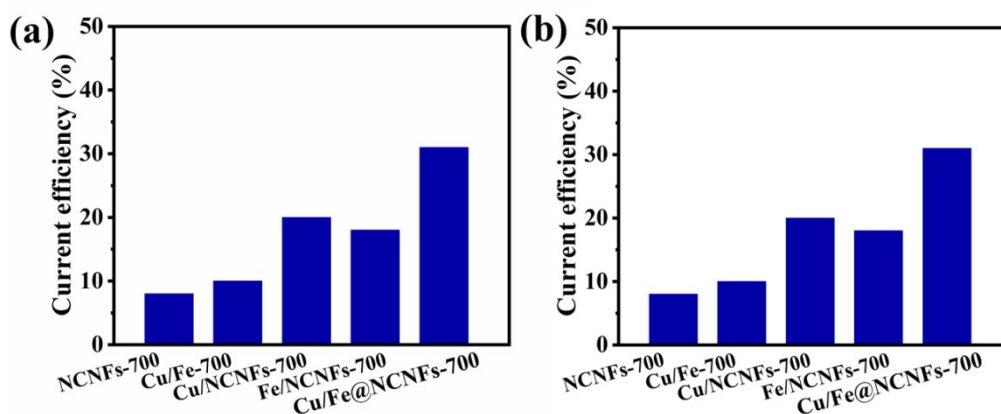


Figure S9. Current efficiency of different samples of Cu/Fe@NCNFs-500, Cu/Fe@NCNFs-600, Cu/Fe@NCNFs-700, Cu/Fe@NCNFs-800, NCNFs-700, Cu/Fe-700, Fe/NCNFs-700, Cu/NCNFs-700, Cu/Fe@NCNFs-700.

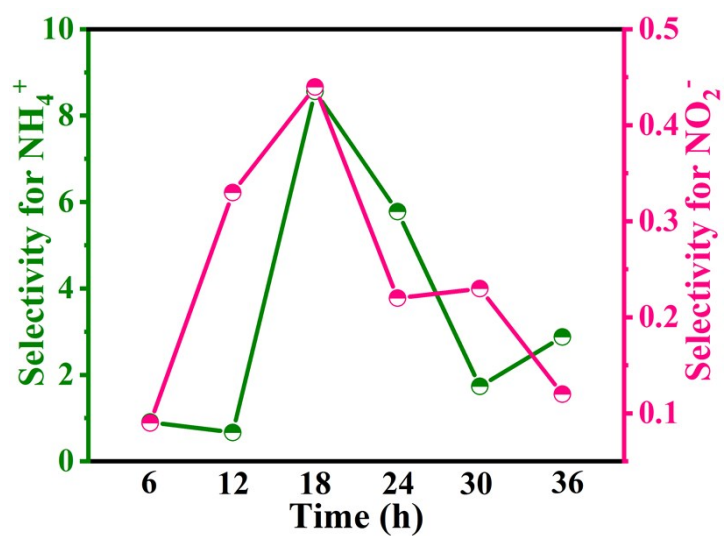


Figure S10. Selectivity for NH_4^+ and NO_2^- of Cu/Fe@NCNFs-700 after 24 h. Testing conditions: initial NO_3^- -N concentration 100 mg L^{-1} ; initial pH value 5; 0.02 M NaCl and $0.1 \text{ M Na}_2\text{SO}_4$.

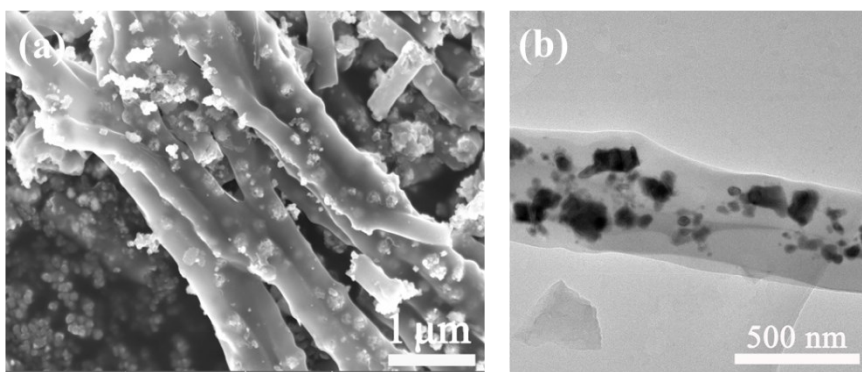


Figure S11. (a) SEM image, (b) TEM image of Cu/Fe@NCNFs-700 before 7 cycles reaction.

Table S1 Nitrate removal capacity of different control samples

Samples	Nitrate removal capacity	Samples	Nitrate removal capacity
Cu/Fe-700	1382 mg N/g Cu/Fe	Fe/NCNFs-700	4500 mg N/g Fe
Cu/NCNFs-700	4154 mg N/g Cu	Cu/Fe@NCNFs-700	5686 mg N/g Cu/Fe

Table S2 The summaries of reported nitrate conversion efficiency of different catalysts.

Materials	Concentration of electrolyte	Conversion efficiency	Ref.
FeNi/g-mesoC/NF	0.05 M Na ₂ SO ₄ +0.02 M NaCl	75%	1
PdCu-OMC	0.1 M Na ₂ SO ₄	28%	2
nZVI@OMC	0.02 M NaCl	~70%	3
Fe/Fe ₃ C-NCNF-2	0.02 M NaCl	33%	4
Cu/Fe@NCNFs-700	0.1 M Na ₂ SO ₄ +0.02 M NaCl	76%	This Work

Table S3 Leached concentration of Cu²⁺ and Fe²⁺ over 7 times electrocatalytic denitrification with Cu/Fe@NCNFs-700.

Cycle times	1	2	3	4	5	6	7
Leached concentration of Cu ²⁺ (mg/L)	0.061	0.060	0.057	0.060	0.063	0.058	0.064
Leached concentration of Fe ²⁺ (mg/L)	0.072	0.075	0.074	0.072	0.078	0.088	0.084

References

1. X. Chen, T. Zhang, M. Kan, D. Song, J. Jia, Y. Zhao and X. Qian, *Environ. Sci. Technol.*, 2020, **54**, 13344-13353.
2. J. Fan, H. Xu, M. Lv, J. Wang, W. Teng, X. Ran, X. Gou, X. Wang, Y. Sun and J. Yang, *New J Chem.*, 2017, **41**, 2349-2357.
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4. Y. Lan, J. Chen, H. Zhang, W.-x. Zhang and J. Yang, *J. Mater. Chem. A*, 2020, **8**, 15853-15863.