## Supporting Information

# Flexible electrocatalysts: Interfacial-assembly of iron nanoparticles for nitrate reduction

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#### **MATERIALS AND METHODS**

#### Synthesis of Fe<sub>3</sub>O<sub>4</sub> NPs.

The uniform size, spherical and monodisperse  $Fe_3O_4$  NPs were synthesized according to the previous literature reports.<sup>1</sup>

#### Fe<sub>3</sub>O<sub>4</sub> NP supraparticles assembly on the carbon cloth.

The commercial carbon cloth was cut to 1 cm × 1 cm specification and then was arranged in 0.2 M oleic acid/n-hexane solution for ligand modification for 12 hours. Subsequently, the modified carbon cloth was placed in a porcelain boat, which added of Fe<sub>3</sub>O<sub>4</sub>/hexane solution with 2 mL to allow the solvent volatilization. The carbon cloth modified with Fe<sub>3</sub>O<sub>4</sub> nanoparticles was carbonized under nitrogen atmosphere at 400 °C for 2 hours to form the carbon coated Fe<sub>3</sub>O<sub>4</sub> interface assembly carbon cloth, which was denoted as CC/Fe<sub>3</sub>O<sub>4</sub>@C. The CC/Fe@C was further prepared by CC/Fe<sub>3</sub>O<sub>4</sub>@C via in-situ thermal reduction treatment under hydrogen atmosphere at 500 °C for 3 hours at a rate of 2 °C/min.

#### Instrumentation.

The morphologies, microstructures of the as-prepared the products were characterized by field-emission scanning electron microscopy (SEM) and high-resolution SEM images were recorded using a Hitachi S4800 microscope operating at 5 kV. Transmission electron microscopy (TEM) images were obtained using a JEM-2100 F microscope operating at 200 kV. The particle size distribution was measured by dynamic light scattering (BI-200SM). X-ray diffraction (XRD) was carried out on a Rigaku D/Max-2550 PC diffractometer (Tokyo, Japan) equipped with Cu Kα

radiation. Iron content in the composite after hydrochloric acid dissolution was determined by Inductive coupled plasma-atomic emission spectrometer (Prodigy-ICP, USA). XPS analyzes using ESCALAB 250Xi.

#### Electrochemical Test and UV Data Analysis.

In a typical three-electrode cell system, platinum (1 cm  $\times$  1 cm) is counter electrode at the position of anode, and saturated mercurous chloride electrode was used as reference electrode to balance the potential. The CC/Fe@C can be firsthand used as the cathode electrode. Electrochemical tests were used on a CHI 660D (Shanghai CHI Instruments Co.) at -1.3 V. Linear Sweep Voltammetry was used to detect the electrocatalytic activity between voltage -2.0 V to 0.0 V.

In addition, sodium nitrate stock solution with different concentration were obtained from initial solution (10 mg/L, 25 mg/L, 50 mg/L, 100 mg/L NaNO<sub>3</sub> was dried for 24h before use). And, single electrolyte system of 0.02 M NaCl, di-electrolyte system of 0.02 M NaCl and 0.02 M Na<sub>2</sub>SO<sub>4</sub>, di-electrolyte system of 0.02 M NaCl and 0.01 M NaCl and 0.01 M Na<sub>2</sub>SO<sub>4</sub>, di-electrolyte, and volume was 50 ml.

Different products are formed including nitrite, nitrous oxide, nitrogen and ammonium when reaction finished.  $N_2$  and other gas products are sparge from solution during traction.  $N_2$  is regarded the generated gas, because the nitrous oxide finally reduced to dinitrogen exclusively with excess hydrogen based on previous reports.<sup>2</sup> The UV-vis spectrophotometer is used for residual concentration detection of nitrate, nitrite and ammonium with an amount of corresponding detective agent.

Determination of NO<sub>3</sub><sup>-</sup>:

1mL electrolyte was mixed with 1 mL 0.1 M HCl and 1 mL 0.8 wt% sulfamic acid solution. Then dilute the above-mentioned solution to 50 ml. The UV-vis spectrophotometer was used to test the absorption intensity at a wavelength of 220 nm. Determination of  $NO_2^{-1}$ :

A mixture of 20 g p-aminobenzenesulfonamide, 1g N-(1-Naphthyl) ethylenediamine dihydrochloride, 50 mL phosphoric acid, and 250 mL ultrapure water was used as a color reagent. The UV-vis spectrophotometer was used to test the absorption intensity at a wavelength of 540 nm.

#### Determination of NH<sub>4</sub><sup>+</sup>:

1mL electrolyte was mixed with 1 mL potassium sodium tartrate solution and 1 mL Nessler's reagent. Then dilute the above-mentioned solution to 50 ml. The UV-vis spectrophotometer was used to test the absorption intensity at a wavelength of 420 nm.

The nitrate removal capacities R of different materials was calculated by the following equation:  $R = (C_0-C_t) * V / m_{Fe.}$  Where  $C_0 (mg/L)$  and V are the initial concentration and volume,  $C_t$  is the concentration after reaction finished at default time. And  $m_{Fe}$  (g) means the mass of iron in nanocomposites coated on the nickel foam. Efficiency of nitrate removal and the selectivity of product were evaluated by the equation:

$$C(NO_{3}^{-})\% = \frac{[NO_{3}^{-} - N]_{0} - [NO_{3}^{-} - N]_{t}}{[NO_{3}^{-} - N]_{0}} \times 100\%$$

$$S(NO_{2}^{-})\% = \frac{[NO_{2}^{-} - N]_{t}}{[NO_{3}^{-} - N]_{0} - [NO_{3}^{-} - N]_{t}} \times 100\%$$

$$S(NH_{4}^{+})\% = \frac{[NH_{4}^{+} - N]_{t}}{[NO_{3}^{-} - N]_{0} - [NO_{3}^{-} - N]_{t}} \times 100\%$$

$$S(N_{2}) = \frac{[NO_{3}^{-} - N]_{0} - [NO_{3}^{-} - N]_{t} - [NH_{4}^{+} - N]_{t} - [NO_{2}^{-} - N]_{t}}{[NO_{3}^{-} - N]_{0} - [NO_{3}^{-} - N]_{t}} \times 100\%$$

 $[NO_3^--N]_0$  is consistent with  $C_0$ ,  $[NO_3^--N]_t$ ,  $[NO_2^--N]_t$  and  $[NH_4^+-N]_t$  is the concentration at final catalytic time t h.

### Reference

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Fig. S1 TEM image and particle size distribution of oil acid coated  $Fe_3O_4$  nanoparticles.



Fig. S2 TEM image of CC/Fe@C



Fig. S3 A corresponding removal capacity of CC/Fe@C for nitrate electrocatalytic reduction in 0.01 M NaCl and 0.01 M Na<sub>2</sub>SO<sub>4</sub> di-electrolyte system (A) the 50 mg/L nitrate N solution at different reaction time, (B) the different concentration nitrate N solution (mg/L) at 24 h.



Fig. S4 (A) to (C) Low-SEM images and local magnification SEM images, (D) to (F) TEM images and local magnification TEM images and HR-TEM image of CC/Fe@C after electrocatalytic reaction in di-electrolyte system (0.02 M NaCl and 0.02 M  $Na_2SO_4$ ) at 24 h.



Fig. S5 The XRD patterns of CC/Fe@C after electrocatalytic reaction in di-electrolyte system (0.02 M NaCl and 0.02 M  $Na_2SO_4$ ) at 24 h.



g. S6 (A) to (C) The Low-SEM images and local magnification SEM images of

CC/Fe@C after electrocatalytic reaction in di-electrolyte system (0.02 M NaCl and

0.1 M Na<sub>2</sub>SO<sub>4</sub>) at 24 h.

Sample	<b>Reduction conditions</b>	Nitrate conversion / %	Nitrogen selectivity / %	Ref.
Pd <sub>4</sub> Cu <sub>4</sub> @N-pC	-1.3 V vs SCE, 36 h	80	95	3
Fe@C	-1.3 V vs SCE, 24 h	75.9	98	4
Fe(20 %) @N-C	-1.3 V vs SCE, 24 h	83	25	5
CNTs@CNx @Ag-800	-0.29 V vs RHE or -0.9 V vs Ag/AgCl, 30 h	33	100	6
Ti/CNTs/ Cu <sub>5</sub> Pd <sub>5</sub>	-1.3 V vs SCE, 4 h	32	42	7
CC/Fe@C	-1.3 V vs SCE, 36 h	92	82	This work

**Table S1.** The comparison of electrocatalytic performance of different catalysts for nitrate conversion and nitrogen selectivity.

#### References

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