

Supporting Information

**Urea & ammonium fluoride di-nitrogens and Cu & Fe bi-metals co-doped carbon felt as cathode for electro-Fenton degradation to norfloxacin:  $^1\text{O}_2$ -dominated oxidation pathway**

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**Captions:**

## Texts:

Text S1. Preparation of C-CuFe, C-CuFe/FN, C-CuFe/UN

Text S2. Analytical method

Text S3. Testing parameters for characterization

Text S4. Mass ratio of leached metal to metal in original catalyst

## Tables:

Table S1. Comparison of literature on reusability

Table S2. Major intermediates for the degradation of NOR in the C-CuFe/N system

## Figures:

Fig. S1 Proof of Reliability of NOR Testing by UV Spectrophotometer

Fig. S2 Comparison of different anodes

Fig. S3 The ion leaching of neutral and alkaline environment

Fig. S4 Reusability of materials

Fig. S5 XRD and XPS comparison of C-CuFe/N before and after reaction

Fig. S6 Electro-chemical characterization (CV and LSV)

Fig. S7 H<sub>2</sub>O<sub>2</sub> accumulation for each electrode system

## **Text S1. Preparation of C-CuFe, C-CuFe/FN, C-CuFe/UN**

### **Preparation of C-CuFe**

A solution containing 0.007 M of  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  and 0.002 M of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  was prepared, and the hydrothermal reaction was carried out in an autoclave lined with polytetrafluoroethylene (PTFE) together with the pretreated CF at 80°C 5 h to obtain the material with a dark blue metallic color, named C-CuFe.

### **Preparation of C-CuFe/FN**

A solution containing 0.007 M of  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , 0.002 M of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  and 0.007 M of  $\text{NH}_4\text{F}$  (FN) was prepared, and the hydrothermal reaction was carried out in an autoclave lined with polytetrafluoroethylene (PTFE) together with the pretreated CF at 80°C 5 h to obtain the material with a metallic luster, named C-CuFe/FN.

### **Preparation of C-CuFe/UN**

A solution containing 0.007 M of  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , 0.002 M of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  and 0.007 M of  $\text{CH}_4\text{N}_2\text{O}$  (UN) was prepared, and the hydrothermal reaction was carried out in an autoclave lined with polytetrafluoroethylene (PTFE) together with the pretreated CF at 80°C 5 h to obtain the material with a metallic coloration, named C-CuFe/UN.

## Text S2. Analytical method

The concentration of NOR was determined using UV spectrophotometer (UV-5500PLUS, Shanghai Youke Instrumentation Co., Ltd.). NOR showed characteristic ultraviolet adsorption peak at 278 nm and the peak intensity represented linear dependence with the concentrations ( $R^2 = 0.99971$ ), as shown in Fig. S1. Specifically, a sample of 2 mL was taken from the reactor at regular intervals, diluted to 10 mL after passing through a 0.22  $\mu\text{m}$  of filter membrane, and then the absorbance at 278 nm was measured immediately.

The leaching of ferric ions was determined by o-phenanthroline spectrophotometry at 510 nm using a UV-5500PLUS spectrophotometer. At the termination time point of the experiment, 5 mL of sample was taken and placed in a 10 mL cuvette, then 0.5 mL of 10% hydroxylamine hydrochloride solution was added and mixed well, then 1 mL of acetic acid-sodium acetate buffer solution and 0.4 mL of 0.5% o-phthalide solution were added sequentially, and water was added to make it 10 mL, then it was left to stand for 15 minutes and its absorbance was measured. The leaching content of copper ions was determined by flame atomic absorption spectrometry.

The TOC was detected using a TOC analyzer (TOC-VCPH, Shimadzu, Japan).

For electrochemical characterization, the catalyst electrodes prepared in this study were chosen as the cathode, the platinum sheet as the anode, Ag/AgCl as the reference electrode, and the electrolyte was 0.05 M of sodium sulfate solution.

System energy consumption is calculated by the following formula.

$$E_{ED} = \frac{UIt}{\Delta\text{TOC} \cdot V \cdot 3.6}$$

where  $I$  (A) represents the applied current,  $U$  (V) represents the supply voltage,  $t$  (s) represents the reaction time,  $\Delta\text{TOC}$  ( $\text{mg} \cdot \text{L}^{-1}$ ) represents the decaying TOC concentration, and  $V$  (L) represents the reaction volume.

### **Text S3. Testing parameters for characterization**

The accelerating voltage was 3 kV for SEM profile shots and 15 kV for energy spectrum mapping shots. Samples were gold sprayed before testing.

The FTIR test resolution was  $4\text{ cm}^{-1}$  with 32 scans and a wave number range of  $400\text{-}4000\text{ cm}^{-1}$ .

XRD tests were performed over a range of  $10\text{-}70^\circ$  (2 Theta) in  $0.02^\circ$  steps of 35.7 seconds each.

The XPS operated at a voltage of 12 kV, a filament current of 6 mA, a full-spectrum scanning flux energy of 150 eV in 1 eV steps, and a narrow-spectrum scanning flux energy of 50 eV in 0.1 eV steps.

The pore size distribution of the mesopores tested for physical adsorption was analyzed by the BJH method and the specific surface area was calculated by the BET equation.

The electrochemical characterization was performed at a scan rate of 0.02 V/s with a sampling interval of 0.001 V. The scan rate was 0.02 V/s with a sampling interval of 0.001 V.

LC-MS mobile phase A: 0.1% formic acid and B: methanol at a flow rate of 0.25 ml/min and an injection volume of 10  $\mu\text{L}$ . Gradient elution conditions:  $t = 0\text{ min}$ , 98% solvent A, 2% solvent B;  $t = 2\text{ min}$ , 98% solvent A, 2% solvent B;  $t = 6\text{ min}$ , 5% solvent A, 95% solvent B;  $t = 13\text{ min}$ , 5% solvent A, 95% solvent B;  $t = 16\text{ min}$ , 98% solvent A, 2% solvent B;  $t = 20\text{ min}$ , 98% solvent A, 2% solvent B. The mass spectrometer has a capillary temperature of  $320^\circ\text{ C}$  and a scanning range of 200-3000 m/z.

**Text S4. Mass ratio of leached metal to metal in original catalyst**

We used XPS to examine the content of each element in C-CuFe/N, in which elemental Fe accounted for 27.71% (3.456 mg), elemental Cu accounted for 9.97% (1.152 mg), and iron ions were leached out of the system by 0.019 mg, and copper ions were leached out of the system by 0.033 mg. The leached iron ions were less than one hundredth of the iron content in the original catalyst, and the leached copper ions were less than one-thirtieth of the copper content in the original catalyst.

**Table S1. Comparison of literature on reusability**

Samples	Pollutants	Reusability	Literatures
EH-GF	Norfloxacin	5 / 92.8%	[10]
CoFe-NC	Sulfamethoxazole	3 / 71.1%	[43]
CoFe-LDH/CF	Amitriptyline	5 / 90%	[44]
MCF/Fe	Norfloxacin	4 / 100%	[45]
SCZ	Norfloxacin	5 / 88%	[46]
CeO <sub>2</sub> /CuFe <sub>2</sub> O <sub>4</sub> @C-NCNFs-800	Norfloxacin	5 / 96.36%	[47]
NCS-LA	Norfloxacin	6 / 90.24%	[48]
GF-GDEs	Norfloxacin	10 / 88.4%	[49]
xCCA-V	Ciprofloxacin	12 / 70%	[50]
Fe-N-C-700/HEF	Ciprofloxacin	4 / 76%	[51]
C-CuFe/N	Norfloxacin	10 / 90.3%	This study

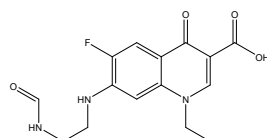
**Table S2. Major intermediates for the degradation of NOR in the C-CuFe/N system**

Number	m/z	Chemical structure	Chemical formula
M0 (NOR)	320		$C_{16}H_{18}FN_3O_3$
M1	302		$C_{16}H_{19}N_3O_3$
M2	318		$C_{16}H_{19}N_3O_4$
M3	334		$C_{16}H_{19}N_3O_5$
M4	332		$C_{16}H_{17}N_3O_5$
M5	336		$C_{16}H_{18}FN_3O_4$
M6	352		$C_{16}H_{18}FN_3O_5$
M7	278		$C_{14}H_{16}FN_3O_2$
M8	336		$C_{16}H_{18}FN_3O_4$



M9

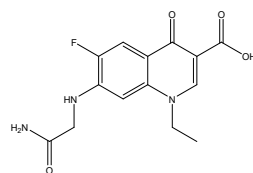
322



$C_{15}H_{16}FN_3O_4$

M10

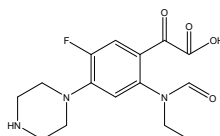
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$C_{14}H_{14}FN_3O_4$

M11

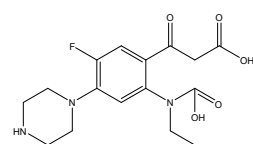
324



$C_{15}H_{18}FN_3O_4$

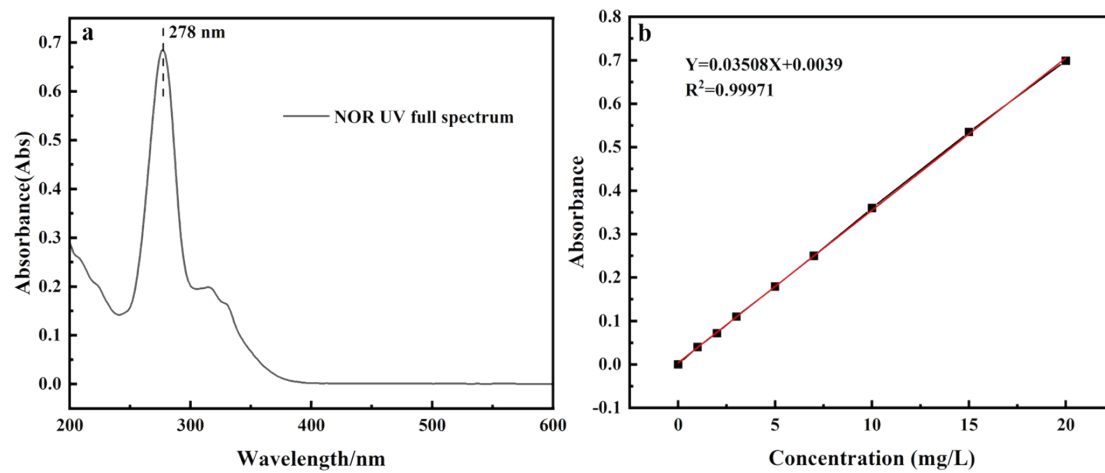
M12

354

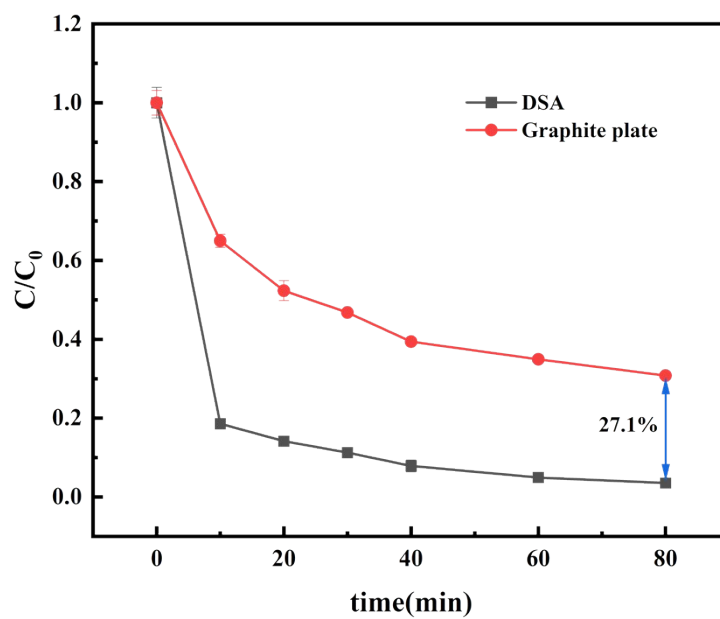


$C_{16}H_{20}FN_3O_5$

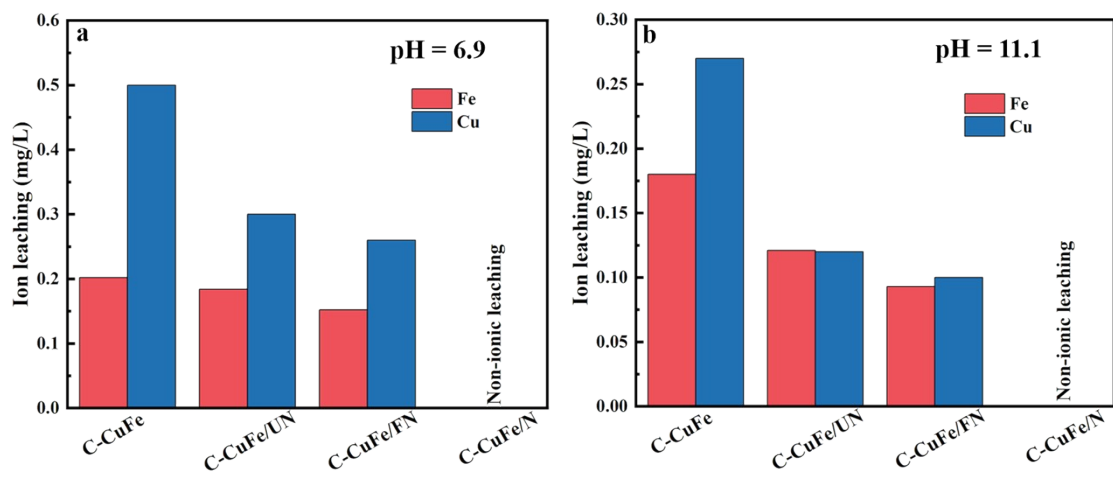
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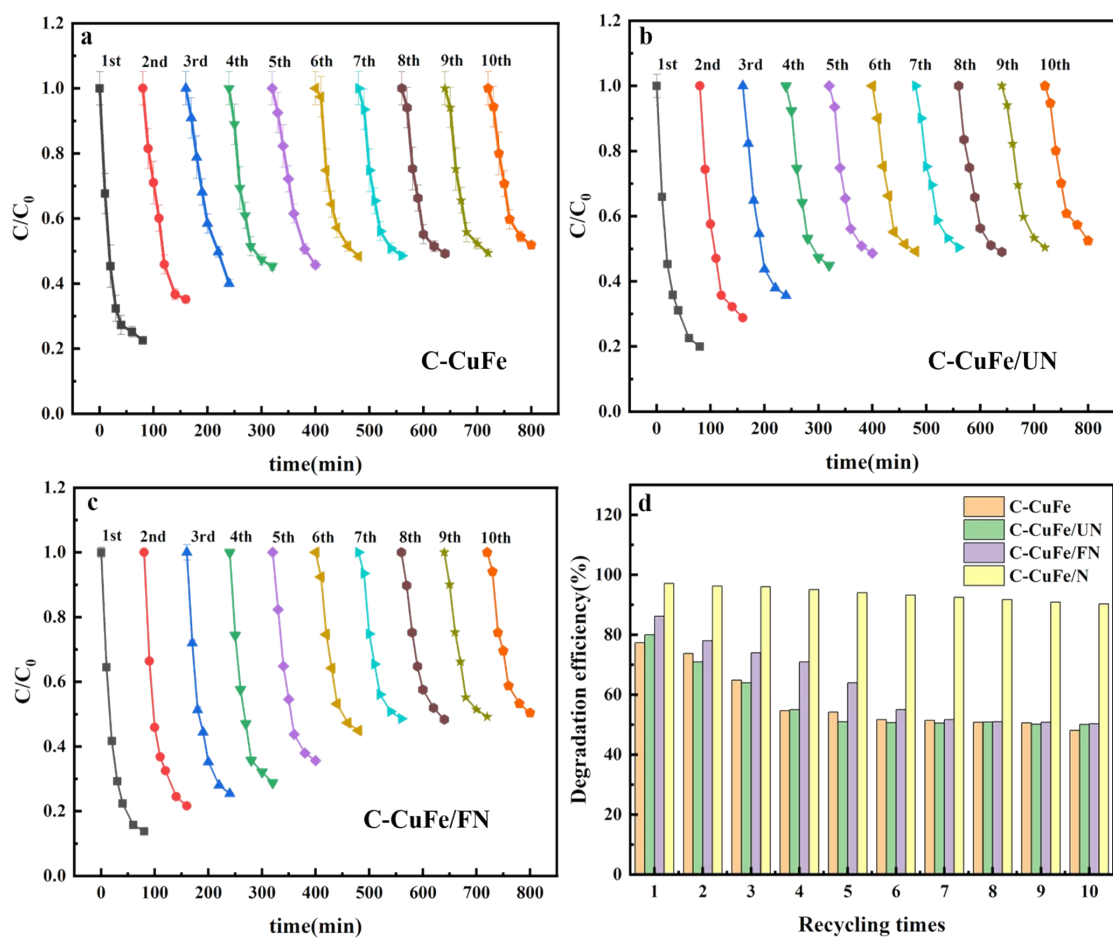
**Fig. S1** (a) UV-vis scanning spectrum of NOR and (b) the linear dependence between the peak intensity at 278 nm with the concentrations



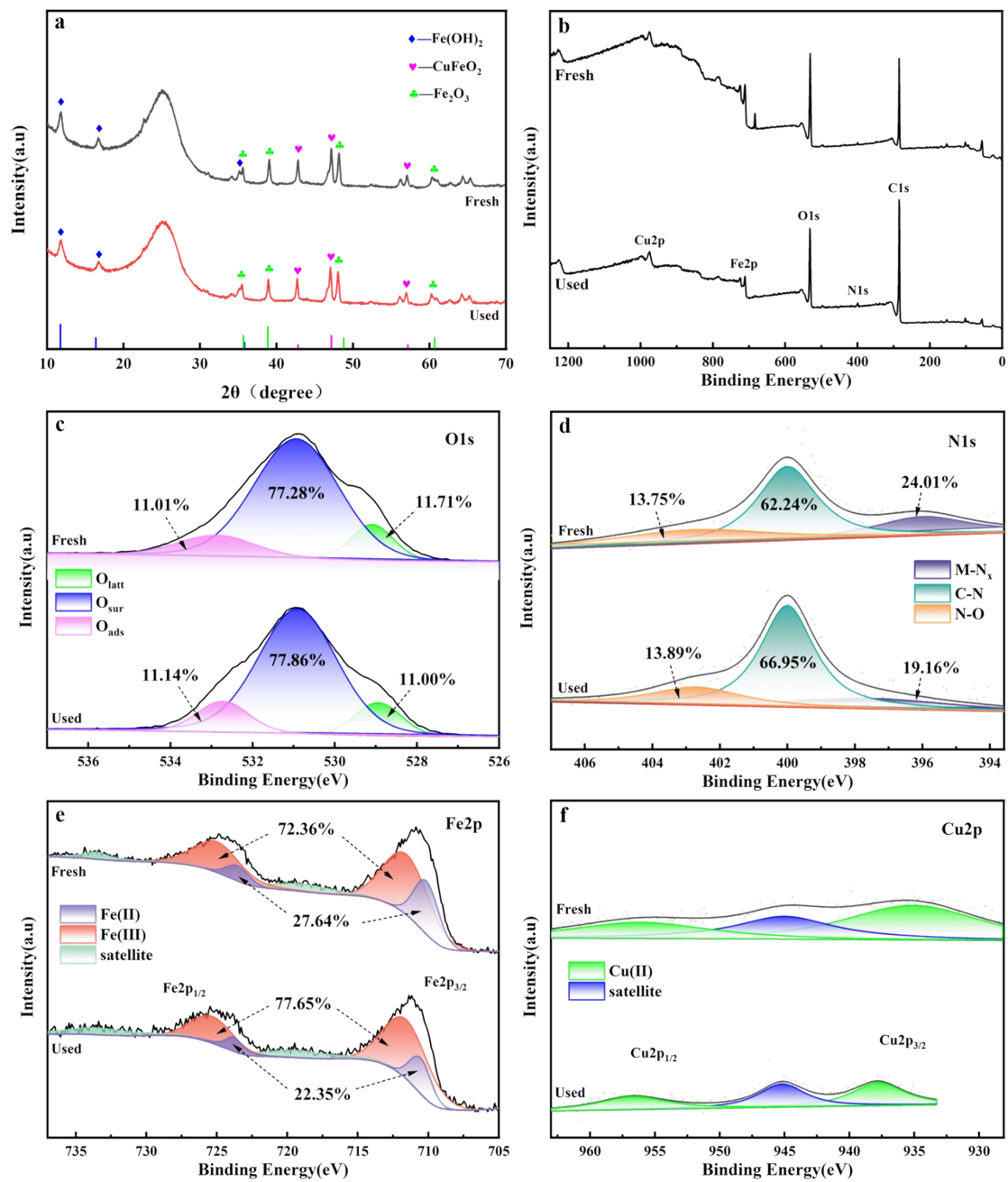
**Fig. S2** Comparison of different anodes



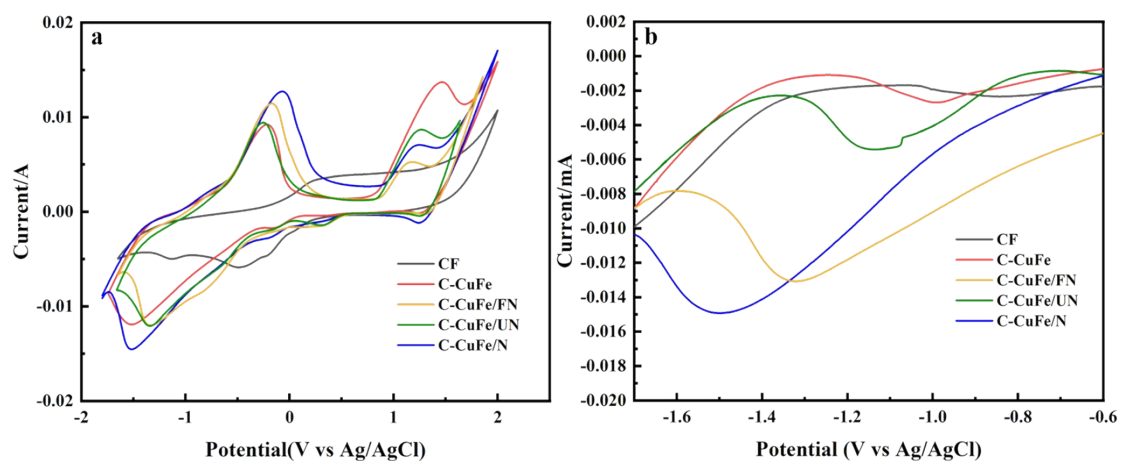
**Fig. S3** (a) Ion leaching under (a) pH = 6.9 and (b) pH = 11.1



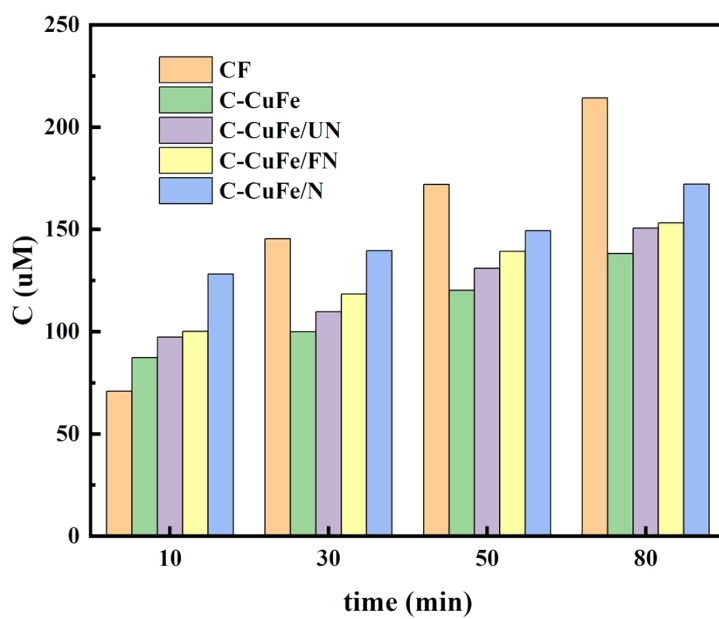
**Fig. S4** The reusability of (a) C-CuFe (b) C-CuFe/UN (c) C-CuFe/FN and (d) Comparison of materials



**Fig. S5** C-CuFe/N before and after the reaction (a) XRD spectra and XPS spectra (b) Full spectrum (c) O1s (d) N1s (e) Fe2p (f) Cu2p



**Fig. S6** (a) CV curves and (b) LSV curves of different samples



**Fig. S7**  $H_2O_2$  accumulation for each electrode system