

Supporting Information

Cu^{II}porphyrin Mediated M-N-C Single- and Dual-Metal Catalysts for Efficient NO₃⁻ Electrochemical Reductions

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Supporting information includes chemicals and materials, preparation of catalysts, detection of the concentration of each ion in the solution, details of pseudo-first-order kinetic model, calculations of electrical energy utilization efficiencies, calculation of the corrosion current density, calculation of the effective area.

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Fig. S2. Raman spectra of rGO and Cu-N-C-t (t= 700/800/900).

Fig. S3. CV curves of (a) Cu-N-C and (b) Cu_{0.8}Ni_{0.2}-N-C at different scan rates from 20 mV s⁻¹ to 100 mV s⁻¹. (c) Liner fitting of the capacitive currents of the catalysts vs scan rates.

Fig. S4. Electrochemical impedance spectra of Cu-N-C and Cu_{0.8}Ni_{0.2}-N-C.

1. Chemicals and materials

Analytical grade pure reagents anhydrous sodium sulfate, ammonium chloride, sodium salicylate, trisodium citrate, isopropanol, acetone, anhydrous ethanol, sodium hydroxide, Nafion solution, sulfamic acid, 1-naphthylamine, and reduced graphene oxide were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. Sulfanilic acid was purchased from Shanghai Yien Chemical Technology Co., Ltd. Sodium nitroprusside dihydrate was purchased from Shanghai D&B Biological Science and Technology Co. Ltd. Tetraphenyl iron porphyrin was purchased from Alfa Aesar (China) Chemical Co., Ltd. Nickel-, manganese-, zinc-, cobalt- and copper-porphyrins were synthesized by experiments. All commercial chemicals used in this experiment were not further purified. Deionized water was used in all experiments.

2. Preparation of Catalysts

2.1 Preparation of Cu-N-C

First, 15 mg of CuTPP were dissolved in 15mL dichloromethane solution via sonicating for 15 min to form a clear solution. 10 mg of rGO was then added and sonicated together for 30 min to obtain a suspension. The mixture was stirred continuously at room temperature for 12 hours. After dried on a rotary evaporator, the obtained powder was placed in a porcelain boat and annealed in the tube furnace with pure Ar flow. Pyrolysis temperature procedure was set as follows: firstly, raise the temperature to 500 °C at the rate of 5 °C min⁻¹; then continue to raise the temperature to t °C (t = 700/800/900) at the rate of 10 °C min⁻¹; afterwards, maintain the temperature for 2 hours, then lower the temperature to 500 °C at the rate of 10 °C min⁻¹, continue to lower the temperature to 300 °C at the rate of 5 °C min⁻¹, and then wait for it to cool naturally to room temperature. And finally, washed for several times with deionized water and isopropanol, and dried on a rotary evaporator to eventually obtained Cu-N-C-t (t= 700/800/900).

2.2 Preparation of Cu_xM_(1-x)-N-C (M=Fe/Co/Ni/Zn/Mn)

Control the mass ratio of NiTPP to CuTPP at 5%, 10%, 20% and 30% to prepare

$\text{Cu}_x\text{Ni}_{(1-x)}\text{-N-C}$ ($x=0.95, 0.9, 0.8, 0.7$) according to the same method as that for Cu-N-C.

3. Detection of the concentration of each ion in the solution

3.1 Detection of the nitrate ion concentration

The NO_3^- in the standard and test samples were tested by spectrophotometry. Nitrate contains the $-\text{N}=\text{O}$ group, which is strongly absorbed in the UV region, and the relationship between the absorbance and its content complies with the Lambert-Beer law, so it can theoretically be determined by UV spectrophotometry. 5% sulfamic acid solution was added to different nitrate concentrations and the absorbance was tested in **Fig S1. (a-b)**.

3.2 Detection of the nitrite ion concentration

The NO_2^- produced by electrocatalytic reduced nitrate roots was detected by a diazo-coupling reaction with UV-visible spectroscopy. Sulfanilic acid solution and 1-naphthylamine solution was added to the nitrite solution at different concentrations, and the absorbance of the solution was tested with a UV-visible spectrophotometer, as shown in **Fig S1. (c-d)**.

3.3 Detection of ammonia ion concentration

The NH_4^+ generated by electrochemical catalyzed reduction of nitrate was detected by indigo blue UV-visible spectroscopy. After staining with indophenol indicator during 2 h incubation, the absorbance of the solution was tested using a UV-visible spectrophotometer, as shown in **Fig S1. (e-f)**.

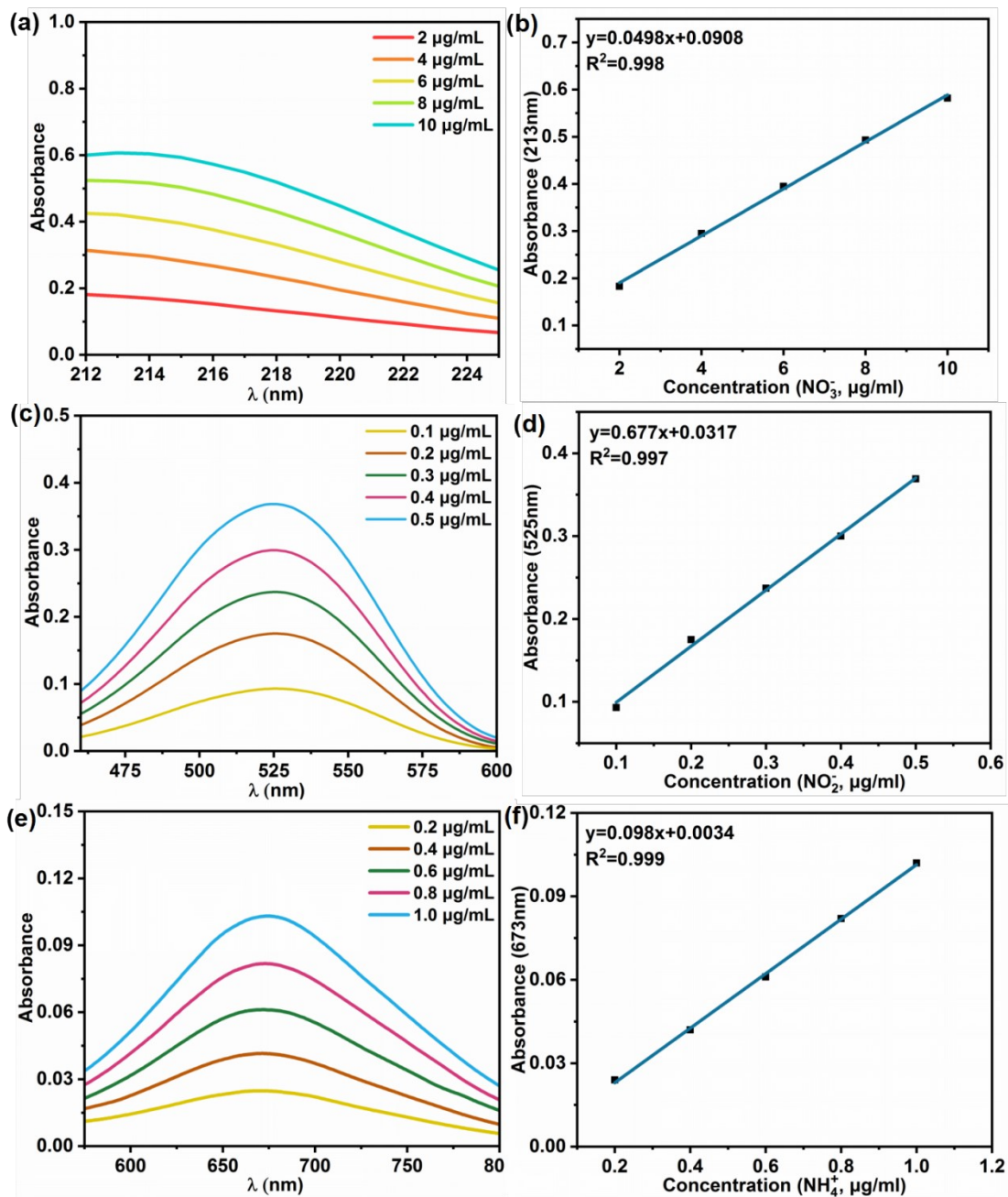


Fig. S1. (a) UV-vis absorption spectra of the different concentrations of NO_3^- solution. (b) Calibration curve for calculating the NO_3^- concentration. (c) UV-vis absorption spectra of different concentrations of NO_2^- solution. (d) Calibration curve for calculating the NO_2^- concentration. (e) UV-vis absorption spectra of the different concentrations of NH_4^+ solution. (f) UV-vis absorption spectra of different concentrations of NH_4^+ solution.

4. Pseudo-first-order kinetic model

Fitting of nitrate reduction over time is shown with a pseudo-first-order kinetic model,

expressed as in eq (S1).

$$\ln(C_f/C_0) = -kt \quad (\text{S1})$$

where C_f is the nitrate concentration at the end of the reaction, and C_0 is the nitrate concentration at the initial reaction time; k is the rate constant of the pseudo-first-order model (h^{-1}), and t is the reaction time.

5. Calculations of electrical energy utilization efficiencies

Based on the removal amount of nitrate and the generation amount of nitrite, ammonia, and N_2 , the electrical energy utilization efficiencies were calculated by eqs. (S2-S5).

$$\eta = [(Q(\text{NO}_2^-)_f) + Q(\text{N}_2)_f + Q(\text{NH}_4^+)_f]/Q_f \quad (\text{S2})$$

$$Q(\text{NO}_2^- - \text{N})_t = 2F(C(\text{NO}_2^-)_f V/M) \quad (\text{S3})$$

$$Q(\text{NH}_4^+ - \text{N})_t = 8F(C(\text{NH}_4^+)_f V/M) \quad (\text{S4})$$

$$Q(\text{N}_2 - \text{N})_t = 5F[(C(\text{NO}_3^-)_0 - C(\text{NO}_3^-)_f - C(\text{NO}_2^-)_f - C(\text{NH}_4^+)_f)V/M] \quad (\text{S5})$$

where η (%) is the electrical energy utilization ratio. Q_f is the total number of electrons during the reaction, which can be checked in the electrochemical workstation. $Q(\text{NO}_2^- - \text{N})_t$, $Q(\text{NH}_4^+ - \text{N})_t$ and $Q(\text{N}_2 - \text{N})_t$ (C) are the electrons during the nitrate reaction at time t ; $C(\text{NO}_3^-)_0$ (mg/L) is the initial concentration of nitrate; $C(\text{NO}_3^-)_f$, $C(\text{NO}_2^-)_f$ and $C(\text{NH}_4^+)_f$ are the concentrations of nitrate, nitrite and ammonia at time f ; V is the volume of solution (25 ml); M is the molar mass of N (14 g/mol) and F is the Faraday's constant (96,500 C/mol).

6. Calculation of the corrosion current density

The corrosion current density was determined by tafel plot in the electrochemical workstation, and the corrosion current (Log I (A)) were obtained by extrapolating the cathodic and anodic branches back to the corrosion potentials. Based on the corrosion current, the corrosion current density was calculated by the eq (S6).

$$j_{cor.} = (1000000 * 10^{\wedge} \log I)/S \quad (\text{S6})$$

where $j_{cor.}$ is the corrosion current density ($\mu\text{A}/\text{cm}^2$); S is the effective specific surface

area.

7. Calculation of the effective area

According to the Randle-Sevcik formula(eq. S7), the effective area of the carbon paper can be calculated. Preparation the $K_3Fe(CN)_6$ solution (including 0.1 mol/L KCl) with 0.01 mol/L. Testing the CV at different sweep speeds in the three-electrode system. Making the I_p - $\nu^{1/2}$ curve, and fit to calculate the electrode effective area.

$$I_p = 268600n^{3/2}ACD^{1/2}\nu^{1/2} \quad (S7)$$

where I_p (mA) is the peak current. n is number of electron transfer; A (cm^2) is the effective area of the electrode, and C (mol/cm^3) is reactant concentration. D (cm^2/S) is diffusion coefficient of the reactants and ν (mV/s) is sweep speeds.

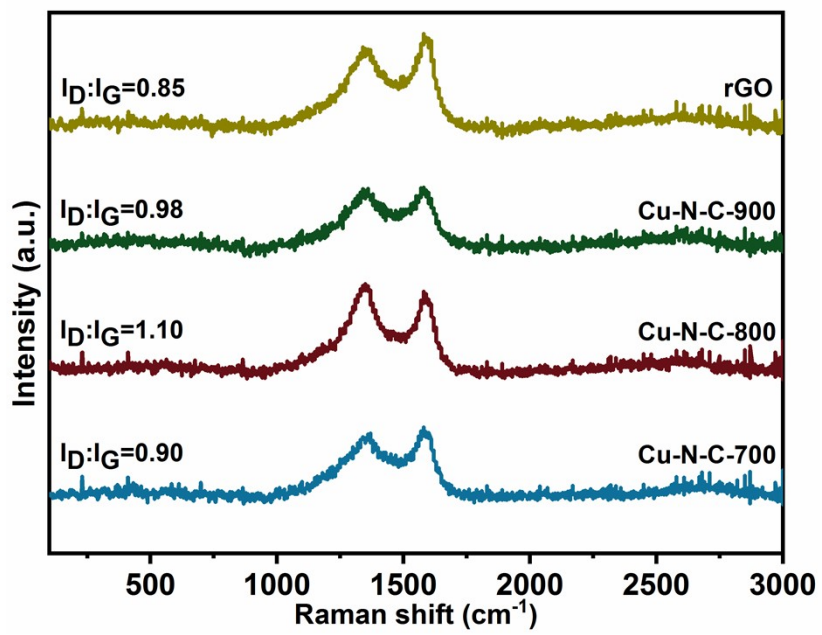


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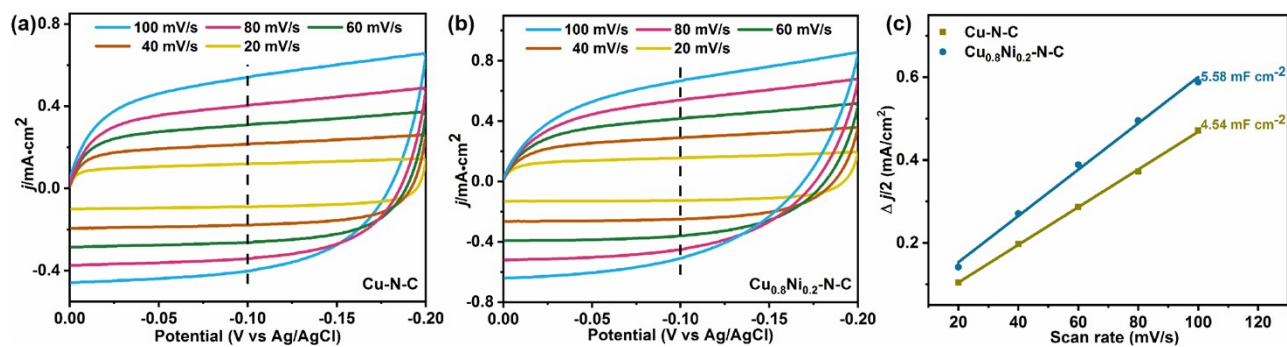


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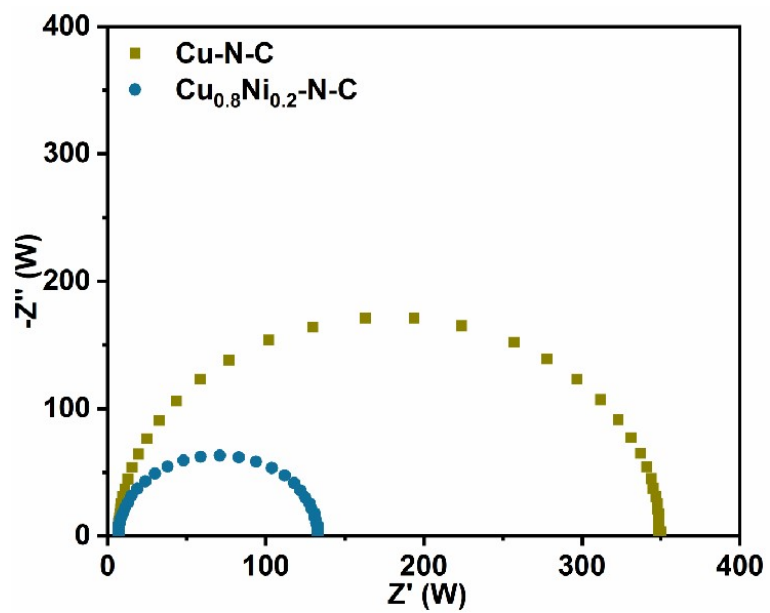


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