Supporting Information

GO regulates bimetallic CoFe catalyst for efficient electrochemical nitrate-to-ammonia under acid conditions

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Contents

1. Materials and Methods

1.1 Chemicals

Potassium nitrate (KNO_3, 99.9%), hydrochloric acid (HCl, 36.0%) and methanol (CH_3OH, 99.9%) were procured from Beijing Chemical Works, while ammonium chloride (NH_4Cl, 99.5%), sodium nitrite ($NaNO_2$, 99%) and phosphoric acid (H_3PO_4) were obtained from Sinopharm Chemical Reagent Co., Ltd. Sulfamic acid (NH_3SO_3), N-(1-Naphthyl) ethylenediamine dihydrochloride ($C_{12}H_{16}Cl_2N_2$), p-aminobenzenesul fonamide ($C_6H_8N_2O_2S$), anhydrous ethanol (C_2H_5OH, $\geq$ 99.5%), cobaltous nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$), ferric nitrate nonahydrate ($Fe(NO_3)_3 \cdot 9H_2O$) and potassium sodium tartrate solution ($C_4H_4KNaO_6$) were all purchased from Adamas-beta Chemical Co., Ltd. Dimethylimidazole ($C_4H_6N_2$) was procured from Aladdin Biochemical Technology Co., Ltd. Nessler's reagent (HgI_4K_2) were acquired from Macklin Inc (China). Nafion solution (5%) was procured from DuPont Company. Carbon cloth was purchased from Carbon Energy Technology Co., Ltd (China). All chemical reagents were used as received without the need for further purification. Deionized (DI) water with a resistivity of 18.2 MΩ·cm was obtained through reverse osmosis, ion exchange and filtration.

1.2 Preparation of GO

GO was prepared from natural graphite powder by a modified Hummer process[1,2]. The 5 mg mL^{-1} GO solution was prepared then stored at room temperature.

1.3 Synthesis of the CoFe$_2$O$_4$/GO catalysts

The CoFe$_2$O$_4$/GO catalysts were successively obtained by solution self-assembly and high temperature annealing methods. 7.5 mL 5 mg/mL GO solution was first mixed with 67.5 mL methanol for 10 min ultrasonic treatment. Then 0.05 mol L^{-1} (M) Fe(NO$_3$)$_3$·9H$_2$O and 0.10 M Co(NO$_3$)$_2$·6H$_2$O were added successively, and ultrasonic treatment was carried out for 10 min each time until completely dissolved which recorded the above mixed solution as solution A. Meanwhile, 0.40 M dimethylimidazole was mixed with 75 mL methanol for 10 min by sonication until dissolved, and the above mixed solution was recorded as solution B. After that, solution B was slowly and evenly poured into solution A, then the mixed solution was self-assembled with 600 rpm magnetic stirring for 6 h at room temperature. The mixture was then centrifuged three times at 10000 rpm for 3 min each time. The bare CoFe$_2$O$_4$/GO powder samples were obtained by cleaning with anhydrous ethanol and drying overnight under vacuum.

The treated bare CoFe$_2$O$_4$/GO powder samples were placed in a crucible and calcined in a tube furnace at 600°C for 2 h in an argon (Ar) atmosphere at a heating rate of 10°C/min. After annealing to room temperature, the products were vacuum dried overnight to obtain the CoFe$_2$O$_4$/GO powder samples. After mixing 5 mg powder with 80 μL DI, 920 μL ethanol and 20 μL 5% Nafion solution, ultrasonic treatment was

carried out for 10 min to obtain ink. Finally, 150 μL ink was evenly drop coating to both sides of the carbon cloth and dried with the aid of infrared lamp to prepare the $CoFe_2O_4$/GO catalysts for electrode treatment.

1.4 Synthesis of the Fe/GO catalysts

The Fe/GO catalysts were successively obtained by solution self-assembly and high temperature annealing methods. 7.5 mL 5 mg/mL GO solution was first mixed with 67.5 mL methanol for 10 min ultrasonic treatment. Then 0.05 M $Fe(NO_3)_3 \cdot 9H_2O$ was added and ultrasonic treatment was carried out for 10 min until completely dissolved which recorded the above mixed solution as solution A. Meanwhile, 0.40 M dimethylimidazole was mixed with 75 mL methanol for 10 min by sonication until dissolved, and the above mixed solution was recorded as solution B. After that, solution B was slowly and evenly poured into solution A, then the mixed solution was self-assembled with 600 rpm magnetic stirring for 6 h at room temperature. The mixture was then centrifuged three times at 10000 rpm for 3 min each time. The bare Fe/GO powder samples were obtained by cleaning with anhydrous ethanol and drying overnight under vacuum.

The treated bare Fe/GO powder samples were placed in a crucible and calcined in a tube furnace at 600°C for 2 h in an argon (Ar) atmosphere at a heating rate of 10°C/min. After annealing to room temperature, the products were vacuum dried overnight to obtain the Fe/GO powder samples. After mixing 5 mg powder with 80 μL DI, 920 μL ethanol and 20 μL 5% Nafion solution, ultrasonic treatment was carried out for 10 min to obtain ink. Finally, 150 μL ink was evenly drop coating to both sides of the carbon cloth and dried with the aid of infrared lamp to prepare the Fe/GO catalysts for electrode treatment.

1.5 Synthesis of the Co/GO catalysts

The Co/GO catalysts were successively obtained by solution self-assembly and high temperature annealing methods. 7.5 mL 5 mg/mL GO solution was first mixed with 67.5 mL methanol for 10 min ultrasonic treatment. Then 0.10 M $Co(NO_3)_2 \cdot 6H_2O$ were added and ultrasonic treatment was carried out for 10 min until completely dissolved which recorded the above mixed solution as solution A. Meanwhile, 0.40 M dimethylimidazole was mixed with 75 mL methanol for 10 min by sonication until dissolved, and the above mixed solution was recorded as solution B. After that, solution B was slowly and evenly poured into solution A, then the mixed solution was self-assembled with 600 rpm magnetic stirring for 6 h at room temperature. The mixture was then centrifuged three times at 10000 rpm for 3 min each time. The bare Co/GO powder samples were obtained by cleaning with anhydrous ethanol and drying overnight under vacuum.

The treated bare Co/GO powder samples were placed in a crucible and calcined in a tube furnace at 600°C for 2 h in an argon (Ar) atmosphere at a heating rate of 10°C/min.

After annealing to room temperature, the products were vacuum dried overnight to obtain the Co/GO powder samples. After mixing 5 mg powder with 80 μL DI, 920 μL ethanol and 20 μL 5% Nafion solution, ultrasonic treatment was carried out for 10 min to obtain ink. Finally, 150 μL ink was evenly drop coating to both sides of the carbon cloth and dried with the aid of infrared lamp to prepare the Co/GO catalysts for electrode treatment.

1.6 Microstructural and chemical characterization

The morphology of the samples was studied via transmission electron microscopy (TEM; Tecnai G2 F20 S-Twin) at an acceleration voltage of 200 kV and scanning electron microscope (SEM, ZEISS Gemini 300). The crystal structures of the samples were characterized via X-ray diffraction (XRD, Rigaku, Smartlab). X-ray photoelectron spectroscopy (XPS) measurements were carried out on a Thermofisher Scientific K-Alpha spectrometer, using Al Kα X-ray radiation (1486.6 eV) for excitation. X-ray spectrometers (EDS) were detected by Oxford Ultim Max 100. In situ attenuated total reflection fourier transform infrared spectroscopy (ATR-FTIR) was measured by Bruker TENSOR II with a resolution of 0.4 cm^{-1} and a beam range from 350 to 8000 cm^{-1}. The ion concentration in solution was measured by UV-Vis absorption spectroscopy (UV-1600, Mapada, China).

1.7 Electrocatalytic measurements of nitrate reduction

The electrochemical measurements were performed using a CHI760E electrochemical workstation (Chenhua, Shanghai) in a cation-exchange membrane separated H-type electrolytic cell. A three-electrode cell system was prepared by using $CoFe_2O_4$/GO (1 cm^2) working electrode and other catalysts. Platinum foil (1 × 1 cm^2) and saturated calomel electrode (SCE) were used as counter and reference electrodes. The dissolved O_2 and N_2 in 0.05 M H_2SO_4 solution electrolyte were purified by argon (Ar, 99.99%) for about 30 min. Cyclic voltammetry (CV) was used for 20 cycles until the working electrode was activated, and a stable CV curve was obtained. Linear sweep voltammetry (LSV) was measured at a sweep rate of 10 mV s^{-1} to remove bubbles, and without stirring during special experiments. The change of materials current response with time under specific voltage was used by chronoamperometry (CA) method. Two flow pumps were employed to circulate a 0.05 M H_2SO_4 solution containing KNO_3 through the cathode and 0.05 M H_2SO_4 solution through the anode chambers respectively, with a flow rate of 20 mL min^{-1}. Ar gas flow was maintained at all times during electrochemical measurements. All polarization curves were not internal resistance (iR) corrected.

For all the electrochemical measurements, the applied potentials have been converted to the reversible hydrogen electrode (RHE) scale by means of the following equation:

$$E_{RHE} = E_{SCE} + 0.059 \times pH + 0.241$$

1.8 UV-Vis spectrophotometry

The concentrations of NO_3^-–N, nitrite (NO_2^-) –N and ammonium (NH_4^+) –N were estimated by UV-Vis spectrophotometry.

Determination of NO_3^-–N

To prepare the solution for analysis, a certain volume of electrolyte was taken and diluted to a final volume of 5 mL within the detection range. Then, 100 μL of 1 M HCl and 10 μL of 0.8 ωt% sulfamic acid solution were added to the solution. The absorption spectrum was analyzed by a UV-Vis spectrophotometer, and the absorption intensities at 200 and 275 nm wavelengths were measured. Using the formula to determine the absorbance value:

$$A = A_{220nm} - 2A_{275nm}$$

Standard potassium nitrate solutions were utilized to create a concentration-absorption curve.

Determination of NO_2^-–N

The nitrite color reagent was prepared as follows: 0.2 g N-(1-Naphthyl) ethylenediamine dihydrochloride, 4 g p-aminobenzenesulfonamide, 10 mL phosphoric acid (ρ = 1.70 g mL^{-1}), and 50 mL DI water were made to a mixture solution. A certain amount of electrolyte was extracted from the electrolytic cell and diluted to 5 mL, which was within the detection range. Subsequently, 100 μL of the color reagent was added to the 5 mL solution and mixed thoroughly before being left to sit for 20 min. The absorption spectrum was measured by an UV-Vis spectrophotometer, and the absorption intensity at 540 nm was recorded. A calibration curve was generated via a range of standard solutions of sodium nitrite to establish the relationship between the concentration and absorbance.

Determination of NH_4^+–N

To prepare the samples for analysis, a certain volume of electrolyte was extracted from the electrolytic cell and diluted to 5 mL to fall within the detection range. Afterwards, 100 μL of potassium sodium tartrate solution (ρ= 500 g L^{-1}) was added to the solution and mixed thoroughly. Then, 100 μL of modified Nessler's reagent was added to the mixture and thoroughly mixed again before leaving it in the dark for 20 min. Finally, the absorption spectrum was measured using an UV-Vis spectrophotometer to record the absorption intensities at 420 nm. Concentration-absorption curves was established using a series of standard ammonium chloride solutions.

1.9 Calculation of other conditional parameters

The faradaic efficiency (FE) for the NH_3 production was defined as charge conversion to NH_3 divided by the total charge passed through the electrodes during the electrolysis (Q), and Q was calculated based on the integration of the curve I (A) vs t (s). Since it was assumed that 8 electrons were required to form an NH_3 molecule, the formula was as follows:

$$FE = (8 \times F \times c \times V) / Q$$

where c represents the measured NH_3 concentration, mmol L^{-1}; V is the volume of H_2SO_4 electrolyte (60 mL), and F is the Faraday constant (96485 C mol^{-1}).

The yield rate (YR) of NH_3 was expressed as equation:

$$YR = (c \times V) / (t \times A)$$

where t is the duration of the electrochemical test, h; and A is the area of the geometrical cathode, cm^{-2}.

The conversion rate of NO_3^- can be expressed in the following formula:

$$Conversion = \Delta C_{NO3-} / C_0 \times 100\%$$

The equations used to obtain the selectivity of NH_3 and NO_2^- are as follows:

$$Selectivity = C / \Delta C_{NO3-} \times 100\%$$

where C_0 is the initial concentration of NO_3^-, ΔC_{NO3-} is the concentration difference of NO_3^- before and after the electrocatalysis, and C is the concentration of each product after the electrochemical test, including NO_2^- and NH_3.

1.10 ECSA evaluation

The ECSA value was in direct proportion to the ratio of double-layer capacitance (C_{dl}) of the working electrode. All catalysts were scanned in 0.05 M H_2SO_4 at the sweep rates of 10, 20, 30, 40, 50 and 60 mV s^{-1}. The potential range was –0.50 to –0.60 V vs. RHE for the $CoFe_2O_4$/GO, Fe/GO and Co/GO. Then, the differential current density for different scanning rate differences was calculated, and a graphical representation corresponding to their respective scanning rates was constructed for each catalyst. Through linear regression analysis, the relationship between current density and scanning rate was derived, and the slope was extracted to determine the double layer capacitance of different catalysts.
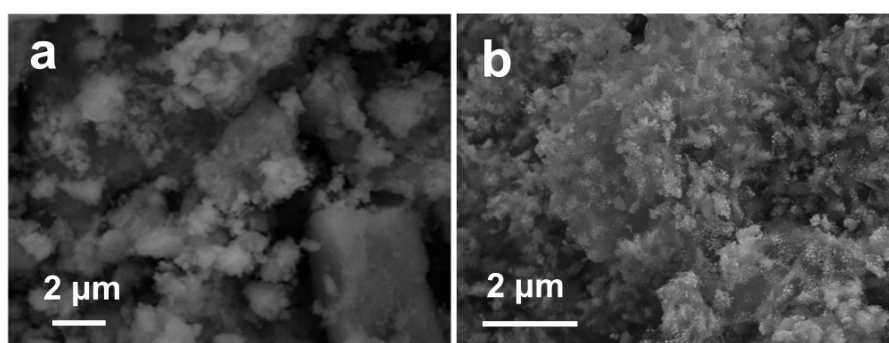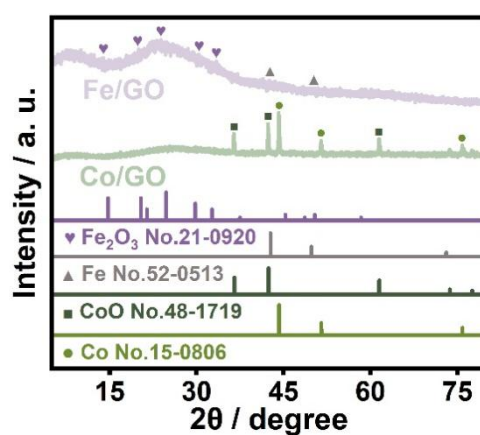
Figure S1. SEM images of (a) Fe/GO and (b) Co/GO.
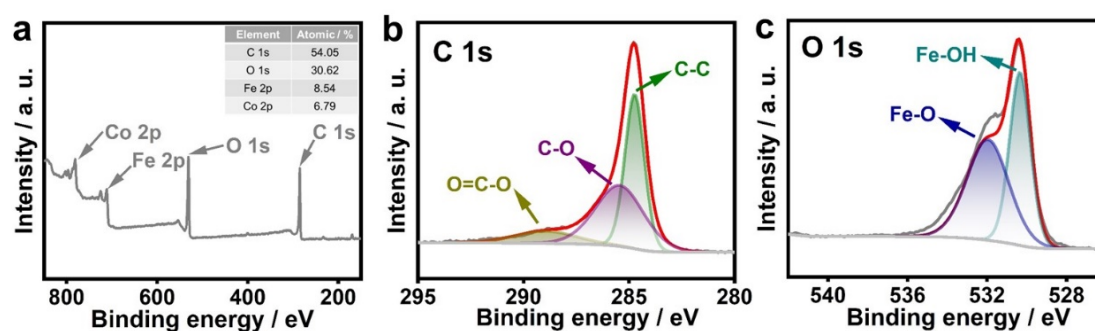

Figure S2. XRD pattern of Fe/GO and Co/GO.

Figure S3. (a) XPS spectrum (inset shows corresponding elements content) and spectra of (b) C 1s and (c) O 1s of $CoFe_2O_4$/GO.

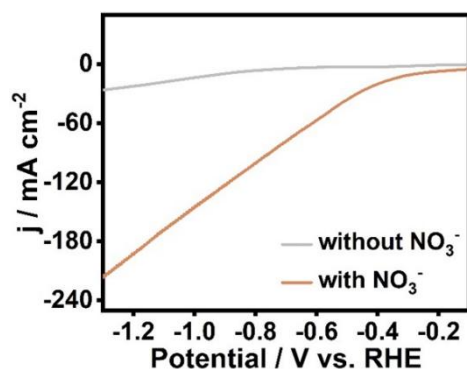**Figure S4.** LSV curves of $CoFe_2O_4/GO$ catalyst in 0.05 M H_2SO_4 solution with and without $NO_3^-–N$.
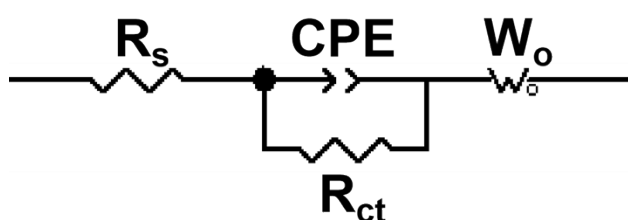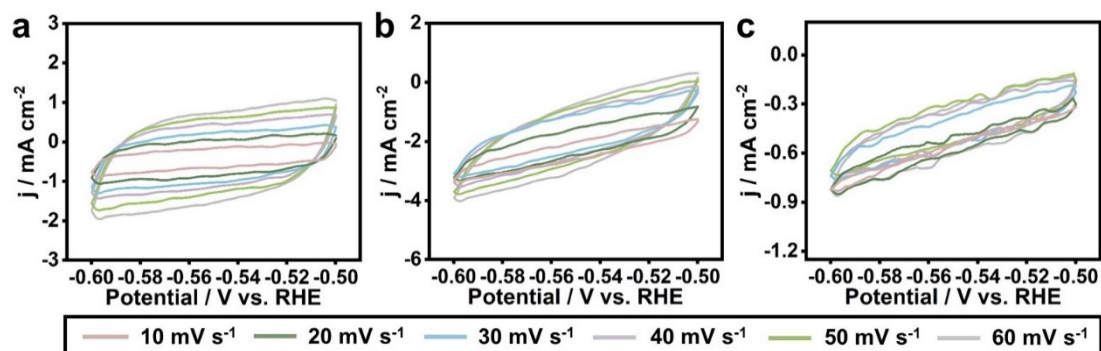

Figure S5. The R(CR)W equivalent circuit model.

Figure S6. CV curves of (**a**) $CoFe_2O_4/GO$, (**b**) Fe/GO and (**c**) Co/GO in 0.05 M H_2SO_4 solution at different sweep rates.
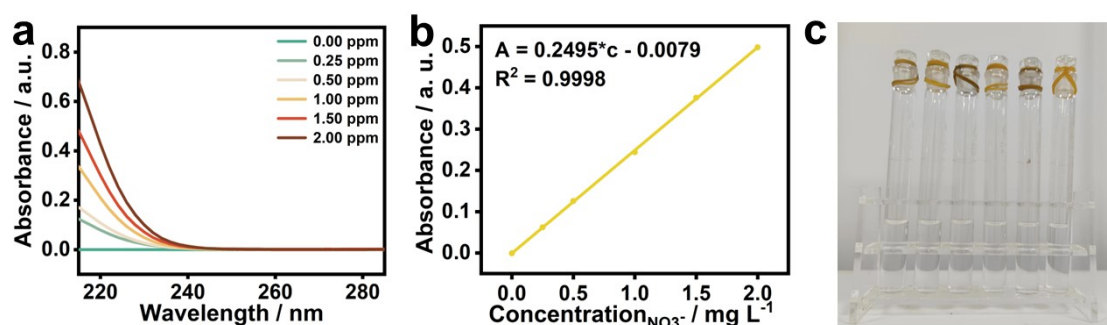

Figure S7. (a) UV-Vis absorption spectra and (b) concentration-absorbance calibration curve of $NO_3^-–N$. (c) Photo of nitrate reactant reagent with increasing $NO_3^-–N$ concentration.
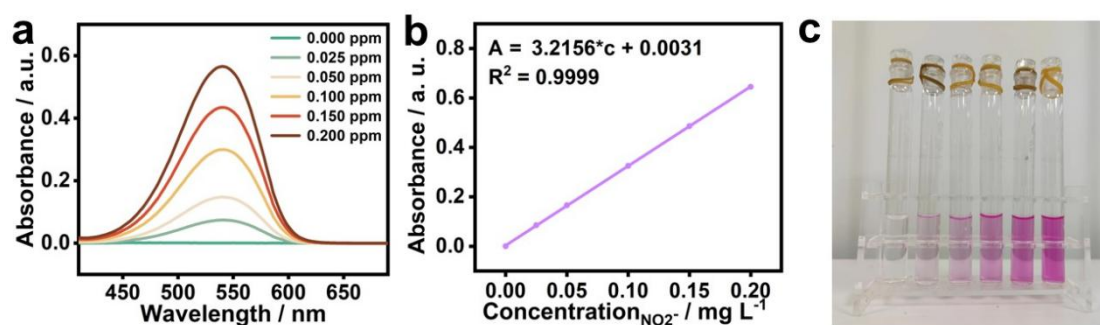
Figure S8. (a) UV-Vis absorption spectra and (b) concentration-absorbance calibration curve of NO_2^-–N. (c) Photo of nitrite colorant reagent with increasing NO_2^-–N concentration.
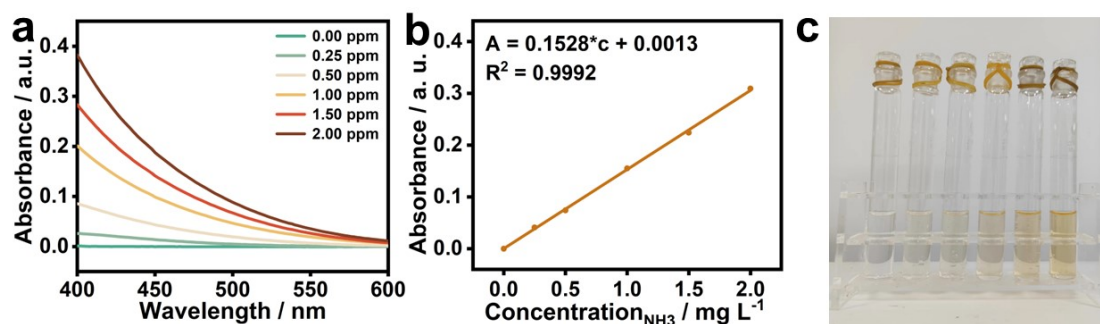

Figure S9. (a) UV-Vis absorption spectra and (b) concentration-absorbance calibration curve of NH_4^+–N. (c) Photo of modified Nessler's reagent with increasing NH_4^+–N concentration.

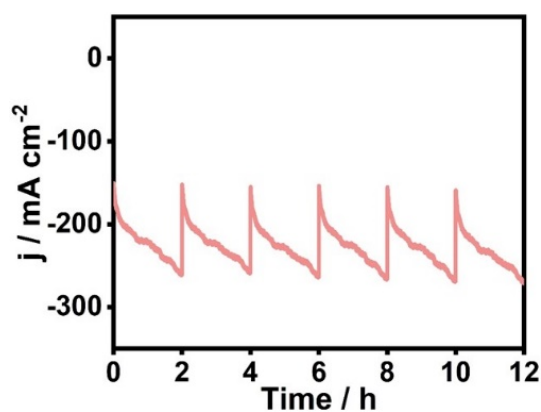**Figure S10.** CA curves of $CoFe_2O_4$/GO catalyst during six consecutive recycling ENRA at −1.3 V vs. RHE in 0.05 M H_2SO_4 solution with 3000 ppm NO_3^-–N.
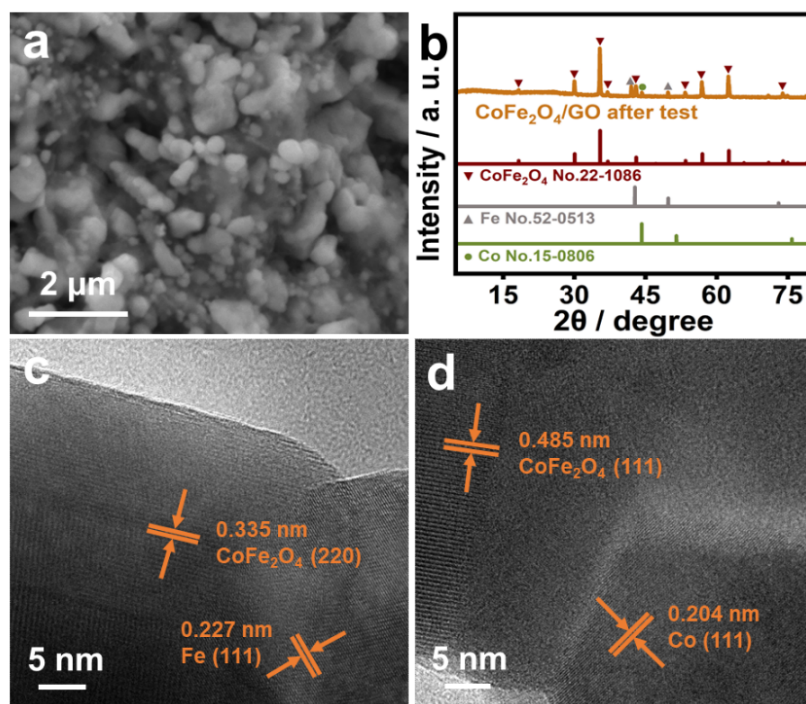
Figure S11. (a) SEM image, (b) XRD pattern and (c, d) TEM images of CoFe$_2$O$_4$/GO catalyst after cyclic test.

Table S1. Comparison of ENRA properties of CoFe$_2$O$_4$/GO and reported catalysts under acidic conditions.

Catalysts	Electrolyte	FE (%)	NH$_3$ yield rate (μmol h^{-1} cm^{-2})	Ref.
CoFe$_2$O$_4$/GO	0.05 M H$_2$SO$_4$ + 0.5 M K$_2$SO$_4$ 0.214 M NO$_3^-$–N	95.51	1268.04	**This work**
Fe$_2$Co-MOF	0.05 M H$_2$SO$_4$ + 0.069 M NO$_3^-$–N	90.55	303.73	3
Ti	0.1 M HNO$_3$ + 0.3 M NO$_3^-$–N	82	108.82	4
Ir NTs	0.1 M HClO$_4$ + 1 M NO$_3^-$–N	84.7	216.71	5
FC	0.05 M H$_2$SO$_4$ + 0.014 M NO$_3^-$–N	20	700	6
F-doped cardon	0.05 M H$_2$SO$_4$	54.8	58.15	7
Ru Sas/GDY/G	0.05 M H$_2$SO$_4$ + 0.5 M Na$_2$SO$_4$	37.6	28.4	8
O-MoC@NC	0.1 mM HCl + 0.5 M Li$_2$SO$_4$	25.1	90	9
Fe-SnO$_2$/CP	0.1 M HCl	20.4	41.35	10
PC/Sb/SbPO$_4$	0.1 M HCl	31	125	11

Note: NO$_3^-$–N not shown in the electrolyte part that not mentioned in the corresponding literatures.

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