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Citation for final published version:

Niu, Shanshan, Qian, Lei-lei, Wang, Yin-yuan, Chu, Guoxiang, Wu, Yingluo, Yang, Ji and Qi, Haifeng 2025. Cu-doped activated Co3O4: tandem site efficient electrocatalytic reduction of nitrate to ammonia. ChemistrySelect 10 (40) , e04759. 10.1002/slct.202504759

Publishers page: https://doi.org/10.1002/slct.202504759

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Supporting Information

Cu-doped activated Co_3O_4: Tandem site efficiently electrocatalytic reduction of nitrate to ammonia

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1. Experimental Section

1.1 Synthesis of ZIF-67

2 g of hydrated cobalt nitrate and 2.25 g of 2-methylimidazole were dissolved in 50 mL of methanol, respectively, then mixed and sonicate for 15 minutes. After standing at room temperature for 3 hours, the solid was separated by centrifugation, washed once with methanol and twice with ethanol, dried overnight.

1.2 Synthesis of Cu-Co_3O_4

A certain amount of copper nitrate (0.05g, 0.1 g, 0.2 g) was dissolved in 40 mL of ethanol, and added 0.5 g of ZIF-67 powder, stirred for 0.5 hour at ambient temperature, centrifuged and washed three times with ethanol, dried overnight, and calcine at 450^{o}C for 0.5 hour in a muffle furnace.

1.3 Synthesis of Co_3O_4

ZIF-67 powder was calcined at 450^{o}C for 0.5 hour in a muffle furnace.

1.4 Material Characterization

The thermal decomposition process of the samples was characterized by Thermogravimetric analysis (TGA, TA-Q50) with heating rate of 10°C/min at N_2 atmosphere. The morphology of the samples was characterized with field-emission scanning electron microscopy (FESEM, Tescan Mira4). Transmission electron microscopy (STEM) images were obtained on the FEI-TALOS-F200X microscope. X-ray diffraction (XRD) analysis was performed on a Smart Lab 9kw diffractometer equipped with a Cu Ka radiation source with a scanning 2θ of 10-80°, operated at 40 kV and 40 mA. Raman analysis was carried out on LabRAM HR 800 Raman Microscope using laser excitation at 532 nm. The surface characteristics of the samples were investigated using Thermo ESCALAB 250 X-ray photoelectron spectrometer (XPS). The content of the elements in the sample is measured by Inductively coupled plasma spectrometer (ICP) (Thermo Kalpha).

1.5 Electrocatalysis test

The performance of electrocatalysts for NO_3^- reduction was evaluated on a CHI660E electrochemical workstation with a three-electrode system in 0.1 M KOH + 0.1M KNO_3 solution. A glassy-carbon (GC) rotating disk electrode (RDE) (d = 6.0 mm) was used as working electrode while a graphite electrode and an HgO electrode were employed as counter and reference electrode, respectively. Before the measurement, the electrolyte was bubbled with Ar flow for 30 min, and continuous Ar flow was maintained during the measurement process. For the activity test, the catalyst sample (2 mg) was ultrasonically dispersed in a mixture of ethanol (0.6 mL), deionized water (0.38 mL) and Nafion (0.02 mL) to form a uniform suspension. A part of catalyst ink (0.020 mL) was then loaded onto the GC electrode, yielding an average mass loading of around 0.2 mg/cm^2. The controlled potential electrolysis was performed at applied potentials for 0.5 h. For long-time stability measurement of Cu-Co_3O_4, other working electrode fabrication and test conditions remained unchanged, time-current curves at -0.7 V *vs.* RHE was tested for 72 hours. Electrochemical impedance spectroscopy (EIS) analysis was performed over the frequency range of 1000 kHz-0.01 Hz and an amplitude of 5 mV. The electrochemically active surface area (ECSA) was measured by using electrochemical capacitance methods. The cyclic voltammograms during 0.67 ~ 0.77 V vs. RHE were firstly conducted with different scan rate of 50-250 mV/s. The electrochemical double-layer capacitance was therefore obtained from the linear slope of the current density against scan rate.

1.6 UV-vis analysis

Different products, such as nitrite and ammonia, can be generated during the reduction of NO_3^-. The ion concentration of the pre- and post-test electrolytes was determined using an

ultraviolet-visible (UV-vis) spectrophotometer. To ensure accurate measurements, the electrolytes were appropriately diluted to match the range of the calibration curves, which are listed below:

1. *Determination of nitrate-N*

4 mL electrolyte was extracted from the electrolytic cell, and adding 1 mL of 0.1 M HCl and 1 mL of 0.8 wt% sulfamic acid, and the resulting solution was diluted to a total volume of 50 mL to match the detection range. For measurement, approximately 5 mL of the uniformly mixed solution was placed in a cuvette, while another 5 mL of deionized water was used as the reference solution in a separate cuvette. The absorption of NO_3^- at wavelengths of 220 nm and 275 nm was then recorded by ultraviolet-visible spectrophotometer. A concentration-absorbance (A_{220}-$2A_{275}$) curve was established using a series of standard nitrate solutions for calibration.

2. *Determination of nitrite-N*

Mix 4 g of p-aminobenzenesulfonamide, 0.2 g of N-(1-Naphthyl) ethylenediamine dihydrochloridee and 10 mL of phosphoric acid (ρ = 1.70 g/mL) and dilute with ultrapure water to 100 mL was obtained to prepare the color reagent. Taking 1 mL of tested electrolyte and adding 9 mL of untested electrolyte, 1 mL of color reagent, stand for 20 minutes. For measurement, above uniformly mixed solution was placed in a cuvette, while another 5 mL of deionized water served as reference solution in a separate cuvette. The absorption of NO_2^- at wavelength of 540 nm was then recorded by ultraviolet-visible spectrophotometer. To establish a concentration-absorbance curve, a series of standard nitrite solutions were employed for calibration.

3. *Determination of ammonia-N*

Typically, the chromogenic agents were prepared as the follows: C#, 1 g sodium nitroferricyanide dehydrate was dissolved into 100 mL H_2O; A#, 6.4 g sodium salicylate and 1.3 g NaOH were dissolved into 100 mL H_2O; B#, 7.5 mL sodium hypochlorite solution and 3.1 g NaOH were dissolved into 100 mL H_2O. The reaction electrolyte with a certain volume were extracted and then diluted to a final volume of 4 mL. Afterwards, 0.32 mL C# solution was added, followed by the addition of 2.4 mL A# and 0.8 mL B# solution. The absorbance of ammonia was measured during 500 ~ 800 nm by ultraviolet-visible spectrophotometer. The ammonia concentration was calculated based on the standard calibration curve (Fig. S7). For measurement purposes, approximately 5 mL of the uniformly mixed solution was placed in a cuvette, while another 5 mL of deionized water served as the reference solution in a separate cuvette. The absorption of NH_4^+ at a wavelength of 655 nm was then recorded. To establish a

concentration-absorbance curve, a series of standard nitrate solutions were employed for calibration.

2. Products calculation

Calculations of NH_3 yield (r_{NH3}) and NH_3 Faraday Efficiency (FE):

$$r_{NH_3} = \frac{n \times V}{t \times A}$$

$$FE = \frac{n \times F \times c \times V}{M \times Q} \times 100\%$$

Where F is the Faraday constant (96485 C/mol), c represents the measured NH_3 concentration, V denotes the volume of the electrolyte (80 mL), M is the molecular mass of NH_3, Q is the total applied charge (C), t is the test time (0.5 h), A is the geometric area of the working electrode (0.2826 cm^2).

3. The adsorption capacity of NO_3^-

To determine the adsorption capacity of NO_3^-, 50 mg of catalyst was added to 25 mL of 0.1M KOH + 0.1 M KNO_3 solution and stirred for three days. The solution was filtered and separated using a 0.45 μm microporous membrane filter. Calculate the adsorption capacity using the following equation:

$$q_e = \frac{(C_0 - C_e) \times V}{m}$$

q_e is the adsorption capacity ($g/g_{cat.}$), C_0 represents the initial concentration of NO_3^- (g/mL), C_e is the measured concentration of NO_3^- after the adsorption (g/mL), V is the volume of the electrolyte (mL), m means the mass of the catalyst (g).

4. In situ differential electrochemical mass spectrometry (DEMS) analysis

During the online DEMS tests, a solution containing 0.1 M of NO_3^--N, 0.1 M KOH was continuously circulated through a peristaltic pump-driven electrochemical cell at a constant speed. To eliminate interference from other components in the air, Ar was continuously injected throughout the test. To establish a stable baseline, LSV tests were conducted from 0.2 to -1 V *vs.* RHE at a scan rate of 5 mV/s. The differential mass signals appeared as gaseous products formed on the electrode surface, and returned to baseline once the electrochemical LSV process concluded. To mitigate any potential accidental errors, three successive LSV tests were performed under identical conditions.

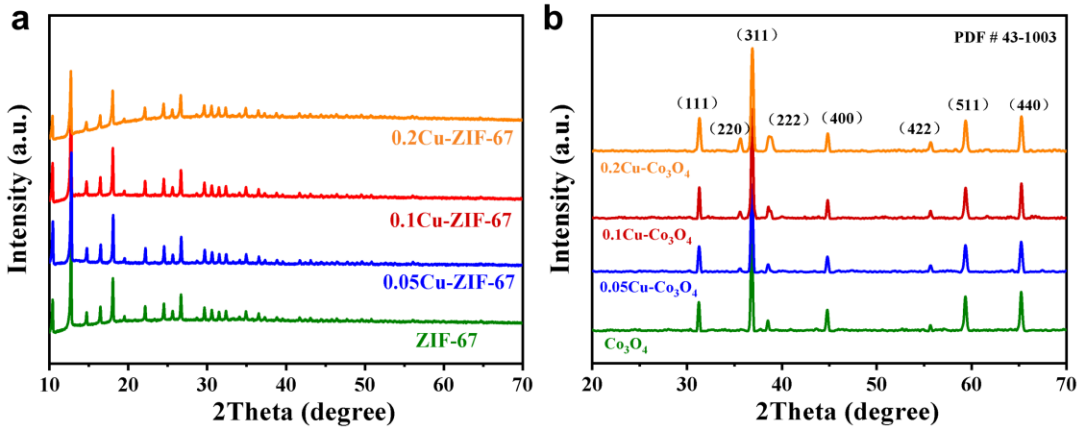

Figure S1. XRD patterns of (a) ZIF-67, 0.05Cu-ZIF-67, 0.1Cu-ZIF-67, 0.2Cu-ZIF-67 samples; (b) Co_3O_4, 0.05Cu-Co_3O_4, 0.1Cu-Co_3O_4, 0.2Cu-Co_3O_4 samples.

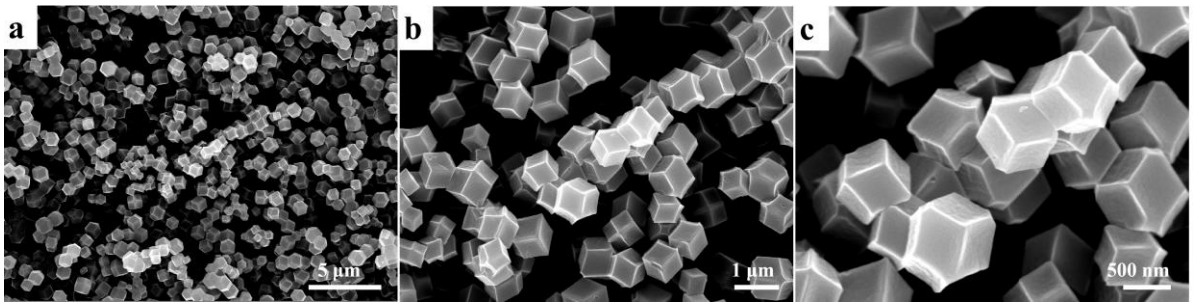

Figure S2. SEM images of the ZIF-67 samples.

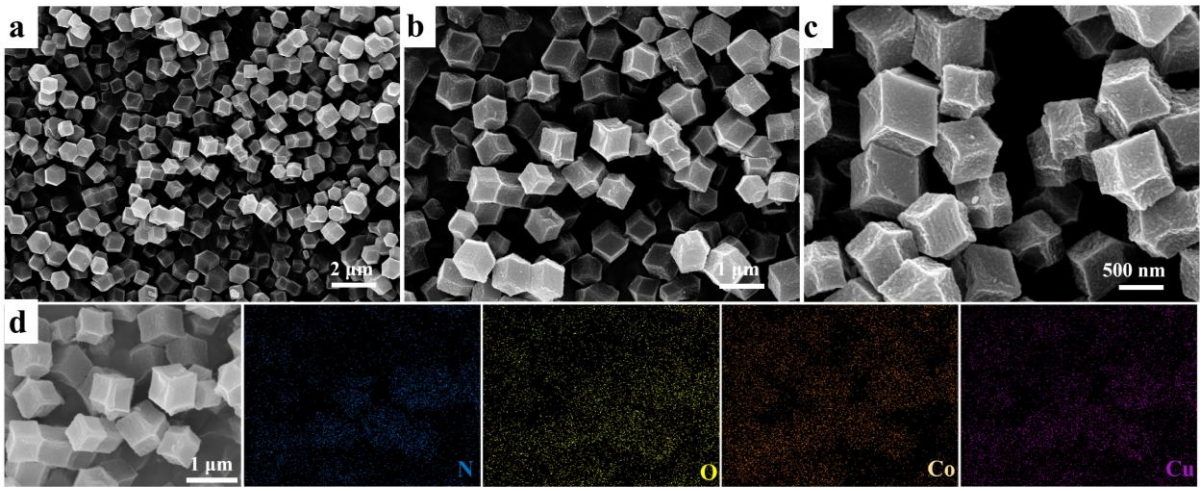

Figure S3. SEM images of the 0.1Cu-ZIF-67 samples.

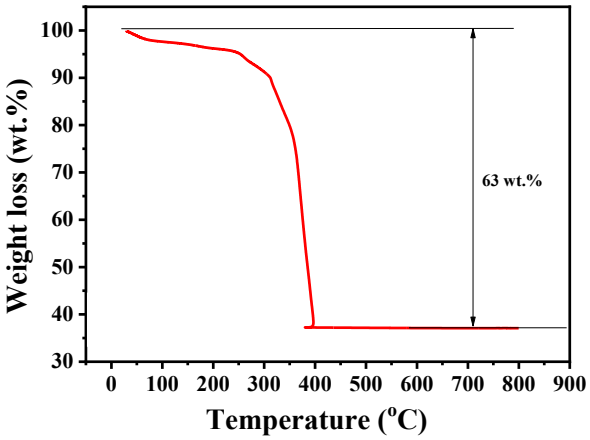

Figure S4. Thermogravimetric curves of the 0.1Cu-ZIF-67 samples in Air.

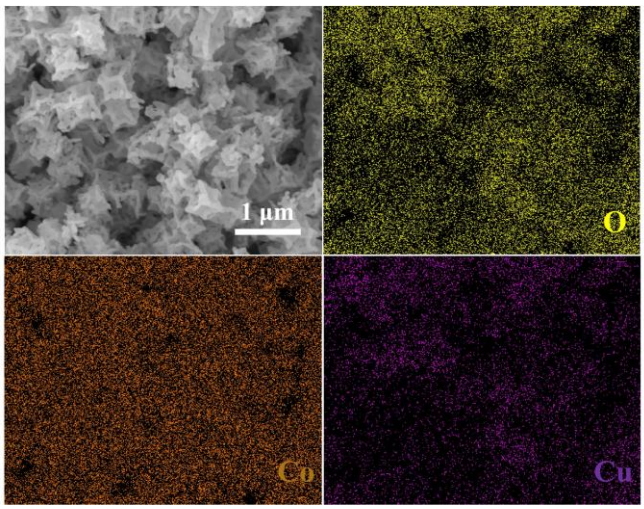

Figure S5. SEM images of the obtained 0.1Cu-Co_3O_4 samples.

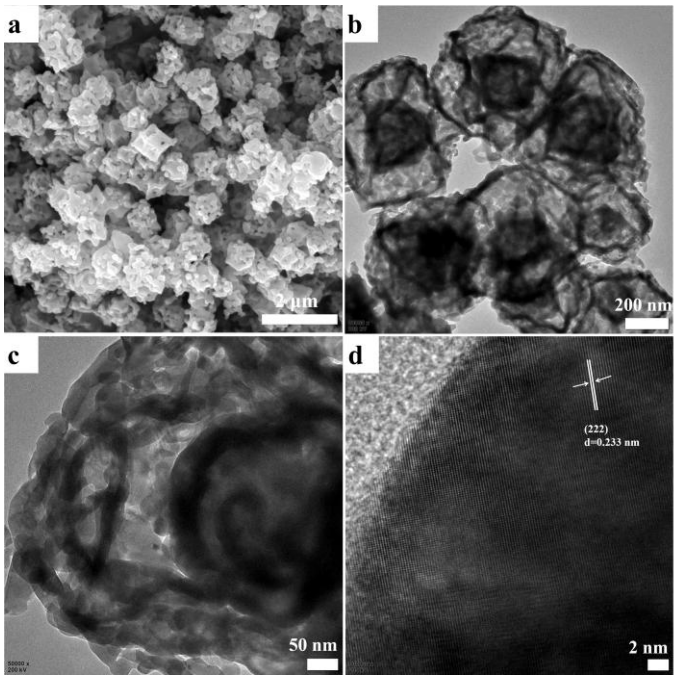

Figure S6. SEM, TEM and HR-TEM images of Co_3O_4.

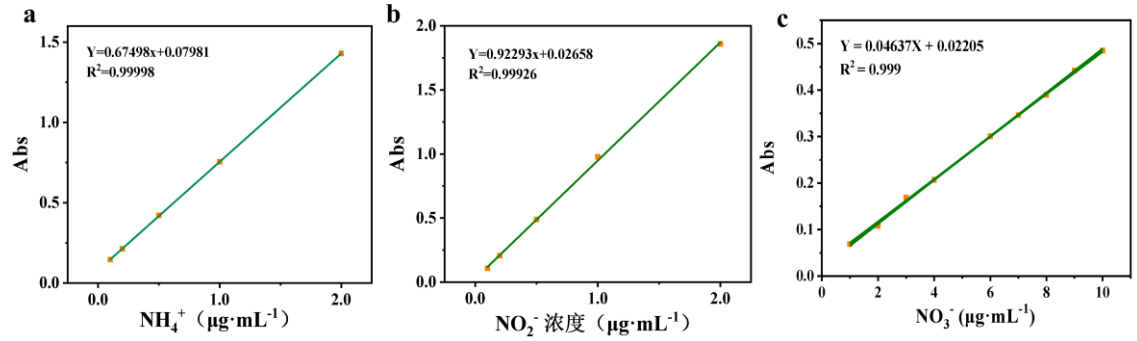

Figure S7. Standard curve of NH_4^+, NO_2^-, NO_3^-.

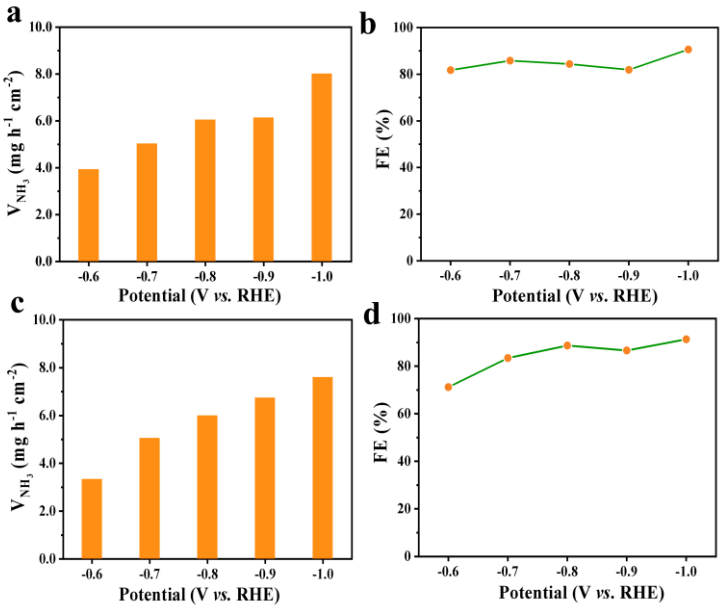

Figure S8. (a) NH_3 yield rates and (b) FE over 0.05Cu-Co_3O_4; (c) NH_3 yield rates and (d) FE over 0.2Cu-Co_3O_4 in 0.1 M KOH aqueous solution with 0.1M KNO_3 at each given potential.

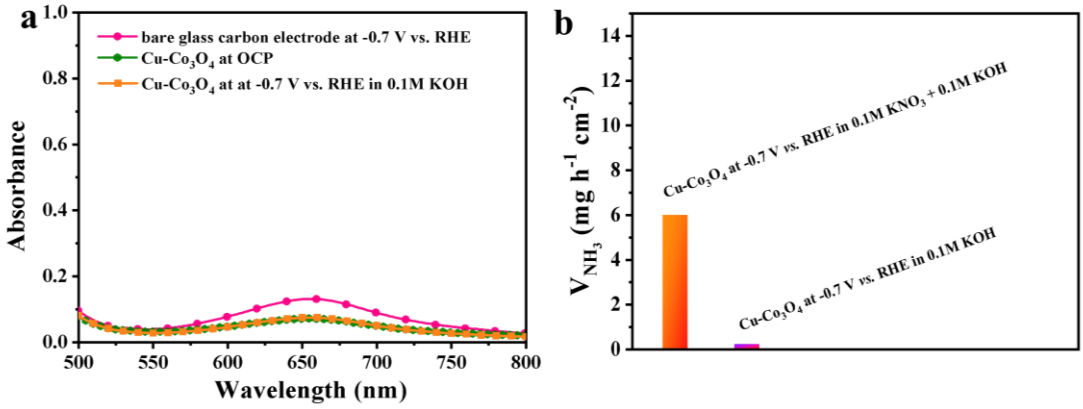

Figure S9. (a) UV-vis spectra of electrolyte after reacting for 0.5 h over bare glass carbon electrode at -0.7 V *vs.* RHE, Cu-Co_3O_4 at open circuit potential, Cu-Co_3O_4 at -0.7 V *vs.* RHE in 0.1 M KOH aqueous solution; (b) NH_3 yield rates over Cu-Co_3O_4 in 0.1 M KOH with or without 0.1 M KNO_3 at -0.7 V *vs.* RHE.