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# Defect-rich Cu@CuTCNQ composites for enhanced electrocatalytic nitrate reduction to ammonia

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#### ARTICLE INFO

Article history: Received 28 February 2023 Accepted 15 May 2023 Available online 25 July 2023

#### Keywords:

Nitrate reduction Ammonia synthesis Copper vacancy Electrocatalysis Electrochemical reconstruction

## ABSTRACT

Electrochemical conversion of nitrate (NO3<sup>-</sup>) pollutants into chemical feedstock and fuel ammonia (NH<sub>3</sub>) can contribute to sustainable mitigation of the current severe energy and environmental crises. However, the electrocatalytic NO3<sup>-</sup> reduction to NH3 (NRA) involves a sluggish multielectron and proton transfer process that competes with the hydrogen evolution reaction (HER) in aqueous media, imposing great challenges in developing highly selective catalysts for NRA. In this study, we developed a copper and copper-tetracyanoquinodimethane composite catalyst (Cu@CuTCNQ), which possesses a high density of copper vacancy defects. This catalyst has been proven to be efficient for NRA through an in situ electrochemical reconstruction method. The structural evolution of CuTCNQ during NRA was investigated by in situ Raman spectroscopy, which indicated an accelerated charge transfer from the CuTCNQ substrate to the derived Cu, which facilitated the adsorption activation of NO<sub>3</sub><sup>-</sup>. The obtained Cu@CuTCNQ exhibited an excellent catalytic performance for NRA, with a Faradaic efficiency of 96.4% and productivity of 144.8 μmol h<sup>-1</sup> cm<sup>-2</sup> at -0.6 V vs. a reversible hydrogen electrode, superior to Cu nanoparticle counterparts and most Cu-based catalysts. Cu vacancy defects and sufficient interfacial charge transfer synergistically optimize the charge distribution of Cu active sites, reduce the energy barrier for  $NO_3^-$  adsorption, and promote deoxidation and hydrogenation processes, thus enhancing NRA and selectivity.

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## 1. Introduction

In recent decades, unrestricted anthropogenic interference, including nitrogen fertilizer loss from over-fertilization in agriculture and improper discharge of industrial and domestic wastewater, has led to excessive accumulation of nitrate ( $NO_3^-$ ) pollutants in surface and groundwater, which has caused an imbalance in the global nitrogen cycle and directly threatens

https://doi.org/10.1016/S1872-2067(23)64454-7



Article

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This work was supported by National Key R&D Program of China (2021YFB4000402), the National Natural Science Foundation of China (52071311, 52273277, 52072362, 21905269), Jilin Province Science and Technology Development Plan Funding Project (20200201079JC, 20220201112GX), Youth Innovation Promotion Association CAS (2021223), and the National Natural Science Foundation of China Outstanding Youth Science Foundation of China (Overseas).

human health and ecosystems [1–3]. The electrochemical conversion of NO<sub>3</sub><sup>-</sup> pollutants into chemical feedstocks and fuels, such as ammonia (NH<sub>3</sub>), using electricity from renewable sources such as solar and wind power is considered a promising approach to alleviate these issues [4–9]. Compared to the current Haber-Bosch method for the large-scale industrial synthesis of NH<sub>3</sub>, this electrochemical method can address issues related to energy-intensive and harsh operations, by coupling with renewable energy sources [10–13]. However, a highly selective electrocatalytic NO<sub>3</sub><sup>-</sup> reduction to NH<sub>3</sub> (NRA) involves multistep proton and electron transfer reactions, which remain as significant challenges for practical applications [14,15]. Therefore, it is crucial to engage in rational design and preparation of highly efficient catalysts.

Currently, Cu is being investigated as a promising non-noble-metal catalysts for the electroreduction of NO3-[16-18]. However, bulk polycrystalline Cu typically exhibits low NH<sub>3</sub> selectivity, with a concurrent competitive hydrogen evolution reaction (HER) [19]. To address this challenge, various strategies have been reported to design efficient Cu-based catalysts for NRA, including morphology modulation, interface construction, tandem effect, alloying effect, and built-in electric field [20-26]. In recent years, in situ characterization techniques have undergone rapid development, enabling the observation of the structural evolution of the catalysts during electrolysis. These techniques have also facilitated the verification of the roles of new highly active phases and local structures generated in situ, such as strain, vacancies, and crystal facets, in triggering efficient catalytic reactions [27-29]. Generally, defective sites not only exhibit exceptional electronic properties but also adjust the electronic structure of adjacent atoms to form new synergistic coordination structures. Thus, the optimal performance of these defect-rich materials was obtained by enhancing the chemical adsorption and altering the energy barriers of the intermediates. These materials have been widely applied in many electrocatalytic reactions such as the OER, ORR, and CO<sub>2</sub>RR [30-33]. The construction of metal-vacancy defect-rich catalysts by structural evolution is anticipated to significantly enhance NRA. However, the influence of metal surface defect engineering on electrocatalytic reactions has not been extensively explored, and the associated reaction mechanism remains unclear [34,35]. Therefore, elucidating the effect of vacancy defects on NRA and reaction mechanism is important for the development of efficient catalysts for NRA.

The advantages of the metal-organic semiconductor copper-tetracyanoquinodimethane (CuTCNQ) include its conductive behavior, charge transfer properties, and ease of reconstruction to form active Cu nanoparticles under reaction conditions [36,37]. Here, the Cu<sup>+</sup> ions in CuTCNQ complexes were partially reduced to vacancy-defect-rich Cu nanoparticles by a facile electroreduction reconstruction approach and distributed uniformly on the remaining reconstituted nanoscale CuTCNQ, giving rise to a highly active Cu@CuTCNQ composite catalyst for NRA. The obtained Cu@CuTCNQ displayed encouraging NRA performance, achieving a maximum NH<sub>3</sub> Faraday efficiency (FE) of 96.4% and productivity of 144.8 µmol h<sup>-1</sup> cm<sup>-2</sup> at -0.6 V, relative to that of a RHE, but better than that of its Cu nanoparticle counterpart. The electrochemical reconstruction of the CuTCNQ microstructures was further characterized using in situ electrochemical Raman spectroscopy. Based on the identification of authentic catalytic sites, intermediate products were detected using online differential electrochemical mass spectrometry (DEMS), and the reaction pathways were deduced using density functional theory (DFT). The results showed that the introduction of Cu vacancies enhanced NO<sub>3</sub><sup>-</sup> adsorption, thereby altering the potential-determining step (PDS) of the electrocatalytic process. This modification led to a reduction in the reaction barrier and inhibited the competing hydrogen evolution reaction, resulting in high NH3 selectivity. This study presents a simple in situ reconstruction strategy to construct efficient NRA catalysts with abundant metal vacancy defects and provides a fundamental understanding of the vacancy defect-dependent activity relationship.

## 2. Experimental

#### 2.1. Chemicals

7,7,8,8-Tetracyanoquinodimethane (TCNQ, 98%), cuprous iodide (CuI 99.95%), and *N*,*N*-dimethylformamide (DMF, 99.5%) were acquired from Shanghai Aladdin Biochemical Technology Co. Ltd. Acetonitrile (CH<sub>3</sub>CN, 99.9%, H<sub>2</sub>O ≤ 50 ppm), dried with molecular sieves, was obtained from Beijing Innochem Technology Co., Ltd. Sodium formate (HCOONa, ≥ 99.0%) and copper acetylacetonate (Cu(acac)<sub>2</sub>, 97%) were purchased from Sigma-Aldrich. Deionized water was obtained from a Milli-Q water integrated system (18.2 MΩ·cm).

#### 2.2. Preparation of CuTCNQ and Cu nanoparticles

## 2.2.1. Synthesis of CuTCNQ powder

In a typical procedure, a 15 mmol L<sup>-1</sup> CuI acetonitrile solution was quickly added to a 10 mmol L<sup>-1</sup> TCNQ acetonitrile solution [38]. To prevent photodecomposition of TCNQ, the mixed solution was stirred in the dark for 10 min. The entire process was performed under an argon atmosphere at room temperature. The resulting dark blue powder of CuTCNQ was collected by filtration, washed with acetonitrile (three times), and dried in an oven at 60 °C.

## 2.2.2. Synthesis of Cu nanoparticles (NPs)

Cu NPs with well-defined crystal structures were synthesized using a facile solvothermal method [39]. Cu(acac)<sub>2</sub> (50 mg), HCOONa (100 mg), and DMF (10 mL) were successively added to a 38-mL pressure vessel and sealed. The homogeneous solution obtained was subsequently heated from ambient temperature to 160 °C using an oil bath and maintained at this temperature for 20 h. Subsequently, the final maroon product was collected by centrifugation and rinsed three times with deionized water.

## 2.2.3. Fabrication of Cu@CuTCNQ electrode

The Cu@CuTCNQ composite was constructed by the in situ

electrochemical reduction reconstruction of the CuTCNQ precursor. First, 5 mg of CuTCNQ powder was dispersed in 5 wt% Nafion (20 uL) and isopropanol (380 uL), which subjected to sonication for one hour to achieve a well-dispersed ink, and then catalyst ink (40 µL) was uniformly dropped onto a carbon paper (CP) substrate (1 × 1 cm<sup>2</sup>), such that a loading of 0.5 mg cm<sup>-2</sup> was obtained. The resulting Cu@CuTCNQ electrode was fabricated as working electrode by performing potentiostatic reduction electrolysis at -0.6 V vs. RHE for 2 h in 0.1 mol L<sup>-1</sup> KOH solution containing 0.1 mol L<sup>-1</sup> NO<sub>3</sub><sup>-</sup>. Ag/AgCl reference and 2 × 2 cm<sup>2</sup> Pt mesh counter electrodes were used.

#### 2.3. Material characterizations

X-ray diffraction (XRD) was performed using a Japan Rigaku D/max-2500 pc instrument with monochromatic Cu  $K_{\alpha}$  radiation ( $\lambda$  = 1.5406 Å). The morphologies and microstructures of the samples were characterized using scanning electron microscopy (SEM, FEI Qunta250) and transmission electron microscopy (TEM, FEI Tecnai G2 F20). X-ray photoelectron spectroscopy (XPS) measurements were performed using a Thermo VG Scientific ESCALAB 250 spectrometer. Cu K-edge X-ray absorption spectra (XAS) were obtained at beamline 1W1B station of the Beijing Synchrotron Radiation Facility. Raman data were collected using a Raman microscope (LabRam HR Evolution) excited with a 633 nm laser. Fourier transform infrared (FTIR) spectroscopy was performed using a Thermo Scientific Nicolet 6700. The absorbance data of the UV-vis spectrometer were obtained using a TU-1901 instrument from Beijing Purkinje General Instrument Co., Ltd. X-band electron paramagnetic resonance (EPR) tests were performed using a Bruker EMXnano EPR spectrometer under liquid-nitrogen cooling.

## 2.4. Electrochemical measurement

A Biologic VMP-300 electrochemical workstation was used for subsequent electrochemical experiments. For the NO<sub>3</sub><sup>-</sup> reduction reaction, 25 mL of a solution consisting of 0.1 mol L<sup>-1</sup> KNO<sub>3</sub> and 0.1 mol L<sup>-1</sup> KOH were added to the cathode and anode chambers separated by a Naffion-212 membrane. Throughout this study, unless explicitly stated otherwise, all potentials measured relative to the Ag/AgCl electrode were converted to the reversible hydrogen electrode (RHE) scale using the formula:  $E_{RHE} = E_{Ag/AgCl} + 0.059pH + 0.197V$ . Chronoamperometry measurements were conducted from -0.4 to -0.8V vs. RHE for 1 h. Linear sweep voltammetry (LSV) tests were performed from 0.3 to -1.0 V vs. RHE at a scan rate of 10 mV s<sup>-1</sup>. For comparison, a Cu electrode was also prepared by drop coating on carbon paper (loading of Cu NPs was comparable to that of Cu in the Cu@CuTCNQ catalyst).

## 3. Results and discussion

CuTCNQ was prepared by reacting CuI with TCNQ in an extra-dry acetonitrile solution, as previously reported. The SEM and TEM images show a micrometer-scale rod-like aggregate morphology (Figs. S1(a)-(c)). A TEM energy-dispersive spectroscopy (EDS) mapping showed a homogeneous distribution of Cu, N, and C over CuTCNQ (Fig. S1(d)). The conductivity of CuTCNQ, measured using a four-point probe method, was 0.18 S cm<sup>-1</sup> (Fig. S2), owing to its strong charge transfer properties. This is in agreement with previously reported values [40]. The chemical structure and XRD pattern of CuTCNQ are shown in Figs. 1(a) and (b), and the latter was refined using the GSAS software. CuTCNQ exhibits a phase I crystal structure with tetragonal symmetry, corresponding to the P-421m space group. The refined lattice parameters are a = b = 11.2357 Å, c = 3.9208Å, and  $\alpha = \beta = \gamma = 90^{\circ}$ . The refined results fit well with the XRD patterns, with  $R_p$  = 3.90%, and  $R_{wp}$  = 5.49%. The crystallographic data are listed in Table S1. The chemical structure of CuTCNQ was characterized by Raman and FTIR spectroscopies (Fig. S3). The typical IR spectral peaks and Raman signals indicate that a pure CuTCNQ phase I sample was synthesized [41,42]. The oxidation state of Cu in CuTCNQ was determined by XPS. Moreover, the Cu 2p spectrum shows Cu  $2p_{1/2}$  and Cu  $2p_{3/2}$  peaks with binding energies of 952.1 and 932.2 eV, respectively, without shoulders or satellites, suggesting the presence of Cu<sup>+</sup> rather than Cu<sup>2+</sup>, as evidenced by the Cu LMM Auger peak at 570.8 eV (Fig. S4). Furthermore, the N 1s spectrum presented a single peak centered at 398.6 eV, indicating the presence of only one N-type TCNQ in the sample [43,44]. XAS was used to further probe the electronic structure of Cu in CuTCNQ. Cu K-edge X-ray absorption near-edge structure (XANES) spectra revealed that the Cu species exhibited an oxi-



**Fig. 1.** (a) Chemical structure of CuTCNQ phase I. (b) XRD and Rietveld refinement patterns of CuTCNQ phase I sample. XANES (c) and FT-EXAFS (d) spectra of Cu K-edge for CuTCNQ and reference samples. Wavelet transform (WT) of EXAFS of Cu foil(e), CuPc (f), and CuTCNQ (g).



Fig. 2. Ex situ SEM characterization for the morphological evolution of CuTCNQ during *in situ* electrochemical reconstruction.

dation state similar to that of the Cu<sub>2</sub>O reference (Figs. 1(c) and S5(a) and (b)). Furthermore, the characteristic peak of CuTCNQ in the first-derivative spectrum of the Cu *K*-edge XANES region was located closer to the Cu(I) position, further confirming the presence of Cu in the oxidation states of Cu(I) in CuTCNQ (Figs. S5(c) and (d)) [45]. In addition, no Cu–Cu bonds were observed in the R-space-extended X-ray absorption fine structure spectrum (EXAFS) (Fig. 1(d)), indicating that Cu<sup>+</sup> was monodispersed in the CuTCNQ complex. A wavelet transform (WT) was performed to analyze the Cu *K*-edge EXAFS oscillations (Figs. 1(e)–(g) and S6). The WT maximum at 4.5 Å<sup>-1</sup>, assigned to the Cu-N coordination in CuTCNQ, is in good agreement with the results of CuPc. Furthermore, with reference to the WT-EXAFS of Cu foil, the absence of an intensity maximum at 7 Å<sup>-1</sup> suggests the absence of Cu–Cu bonds in CuTCNQ.

The Cu@CuTCNQ composites were prepared by electrochemical reconstitution of CuTCNQ in 0.1 mol L<sup>-1</sup> KOH solution (containing 0.1 mol L<sup>-1</sup> KNO<sub>3</sub>) at –0.6 V vs. RHE for 2 h (Fig. S7). *Ex situ* SEM was performed to study the evolution of the morphology at various time intervals during the electrochemical reduction treatment (Fig. 2). When the electrolysis time is between 20 and 40 min, the initial CuTCNQ undergoes a gradual etching from the outside to the inside. This etching is accompanied by the generation of numerous small flakes resembling snowflakes, which remain on the surface and are transferred onto the carbon fiber current collector. As the electrolysis continued, the pristine CuTCNQ was completely reconstituted after approximately 80 min, resulting in the formation of snowflake-like flakes that were tightly wound around the carbon fibers. These flakes remained unchanged even with further extension of the electrolysis time (Fig. S8).

The crystalline structures of the Cu@CuTCNQ composites were confirmed by XRD, as shown in Fig. 3(a). The reconstructed Cu@CuTCNQ exhibited a distinguishable diffraction peak at 43.2°, which was ascribed to the Cu (111) crystal plane (PDF #04-0836). The diffraction peak at 15.5°, assigned to CuTCNQ, remained visible even after reconstruction. Apart from the broad peak in the range of 20°-30°, attributed to carbon paper, no diffraction peaks corresponding to any other Cu-based species or the ligand TCNQ were observed (Fig. S9). To elucidate the electrochemical reconstruction process of CuTCNQ, ex-situ XRD was performed to monitor the structural changes (Fig. S10). During the first 80 min of the reconstruction process, the intensity of the main diffraction peaks of CuTCNQ gradually decreased, accompanied by a gradual enhancement in the diffraction peaks of metallic Cu. When the reaction time was extended from 80 to 120 min, the typical diffraction peaks attributed to CuTCNQ (15.5°) and metallic Cu (43.2°) remained without any alterations in their intensities. This observation confirms that the restructuring of CuTCNQ was almost complete around 80 min, and no significant structural changes occurred upon further prolongation of the reaction time at -0.6 V vs. RHE. The morphologies and internal microstructures of the Cu@CuTCNQ composites were further studied using TEM. Unlike the amorphous structure observed in the TEM images of CuTCNQ (Figs. 3(b), S11(a), and S11(b)), the TEM images of Cu@CuTCNQ clearly show the presence of crystalline nanoparticles on the sample surface (Figs. 3(c) and (d)). A high-resolution transmission electron microscopy (HRTEM) image (Fig. 3(e)) shows an interplanar spacing of 0.205 nm, which is assigned to the face-centered cubic Cu (111) plane. This measurement is in agreement with the XRD results described above. Numerous inconspicuous and discontinuous lattice fringes are observed on the Cu surface, implying the



Fig. 3. (a) XRD patterns of Cu@CuTCNQ composites formed by electrochemical reconstruction of CuTCNQ. (b) TEM image of CuTCNQ. (c,d) TEM images of Cu@CuTCNQ. (e) HRTEM image of Cu@CuTCNQ. (f) Elemental mapping images of Cu@CuTCNQ.

presence of abundant Cu vacancy defects in Cu@CuTCNQ, as marked by the orange dashed boxes. Such prominent lattice defects were prevalent in Cu@CuTCNQ (Figs. S11(c) and (d)). The EPR spectra were further studied for Cu vacancies in Cu@CuTCNQ and Cu NPs (Fig. S12). In contrast to the absence of an EPR signal in Cu NPs with good crystal structure, the reconstituted Cu@CuTCNQ exhibited a significant EPR signal at g= 1.995, confirming the presence of Cu vacancies [46]. The corresponding elemental mapping reveals the distribution of Cu, N, and C in Cu@CuTCNQ (Figs. 3(f) and S13), further confirming the presence of the CuTCNQ substrate.

In a typical three-electrode H-type electrolytic cell, a Cu@CuTCNQ working electrode was used to evaluate the electrocatalytic NRA under ambient conditions. Unless otherwise stated, all potentials were referenced to the RHE without IR compensation. The product NH<sub>3</sub> was quantified by indophenol blue spectrophotometry and further confirmed by <sup>1</sup>H nuclear magnetic resonance (NMR) analysis, and the potential by-product NO<sub>2</sub><sup>-</sup> was measured by ion chromatography (Fig. S14). First, LSV tests were performed in a 0.1 mol L-1 KOH electrolyte with and without KNO<sub>3</sub> to investigate the catalytic behavior of Cu@CuTCNQ for NO<sub>3</sub><sup>-</sup> reduction (Fig. 4(a)). Both CuTCNQ and Cu@CuTCNQ exhibited more positive onset potentials and higher current densities in NO3<sup>-</sup>-containing electrolytes than in their NO3<sup>-</sup>-free counterparts, confirming their catalytic role in electrochemical NO3<sup>-</sup> reduction. The current density of Cu@CuTCNQ was significantly enhanced at the same potential as that of CuTCNQ. When the LSV curves were further normalized by the electrochemically active surface area (ECSA), it can be found that Cu@CuTCNQ exhibited a much larger NO3<sup>-</sup>

reduction current density than CuTCNQ, highlighting its higher NO3<sup>-</sup> reduction activity (Fig. S15). These results verify that Cu is the active site for the NO3- reduction reaction. In contrast to CuTCNQ, Cu@CuTCNQ exhibits two distinct reduction peaks in the scan potential range. The peak located at around -0.15 V vs. RHE was attributed to the conversion of NO2<sup>-</sup> to NH2OH (NO2<sup>-</sup> +  $4H_2O + 4e^- \rightarrow NH_2OH + 5OH^-$ ), while another peak at around -0.7 V vs. RHE was ascribed to the electroreduction of NO2<sup>-</sup> to NH<sub>3</sub> (NO<sub>2<sup>-</sup></sub> + 5H<sub>2</sub>O + 6e<sup>-</sup> → NH<sub>3</sub> + 7OH<sup>-</sup>) [20,47]. To further determine the NRA selectivity of Cu@CuTCNQ, chronoamperometry tests were conducted in 0.1 mol L-1 KOH solution containing 0.1 mol L<sup>-1</sup> NO<sub>3</sub><sup>-</sup>, over a potential range of -0.4 to -0.8 V vs. RHE for 1 h (Fig. 4(b)). Furthermore, to highlight the role of Cu vacancies in Cu@CuTCNQ on improving the NRA selectivity, Cu NP counterparts with good crystal structures were synthesized, and their NO3<sup>-</sup> electroreduction performance was evaluated (Figs. S16 and S17). The change trend in the LSV curve of Cu@CuTCNQ was different from that of CuTCNQ and similar to that observed for Cu NPs, indicating that Cu was the active phase that promoted the NO3- reduction reaction for the Cu@CuTCNQ composites. As the reaction potential becomes more negative, the NH<sub>3</sub> FE of Cu@CuTCNQ show a volcanic trend and reach 96.4% at -0.6 V vs. RHE (Fig. 4(c)), which is better than that of the Cu NPs (79.7%). In contrast, the FE of NO2<sup>-</sup> decreases continuously with decreasing cathodic potential (Fig. S17(c)). Cu@CuTCNQ exhibited a higher NH<sub>3</sub> FE and lower NO<sub>2</sub><sup>-</sup> FE than the those of the Cu NPs over the entire applied potential range, suggesting that Cu@CuTCNQ with Cu vacancy defects is more favorable for NH<sub>3</sub> production. Furthermore, the sum of FE for NH<sub>3</sub> and NO<sub>2</sub><sup>-</sup> was close to 100%



**Fig. 4.** (a) LSV polarization curves of CuTCNQ and Cu@CuTCNQ in 0.1 mol  $L^{-1}$  KOH electrolyte with and without 0.1 mol  $L^{-1}$  NO<sub>3</sub><sup>-</sup>. The scan rate is 10 mV s<sup>-1</sup>. (b) Chronoamperometry curves of Cu@CuTCNQ in 0.1 mol  $L^{-1}$  KOH solution with 0.1 mol  $L^{-1}$  NO<sub>3</sub><sup>-</sup> at various applied potentials. FE (c) and yield rates (d) of NH<sub>3</sub> over Cu@CuTCNQ and Cu NPs in 0.1 mol  $L^{-1}$  KOH electrolyte with 0.1 mol  $L^{-1}$  NO<sub>3</sub><sup>-</sup>. (e) <sup>1</sup>H NMR spectra at various electrolysis time intervals at the applied potential of -0.6 V vs. RHE, using 0.1 mol  $L^{-1}$  KOH containing 0.1 mol  $L^{-1}$  <sup>15</sup>NO<sub>3</sub><sup>-</sup> as the electrolyte. (f) Current density at the applied potential of -0.6 V vs. RHE for 10 h.

over the entire tested potential range, indicating that Cu shows inertness to HER and high activity for the reduction of NO3-[48]. The maximum NH<sub>3</sub> current density (*j*NH<sub>3</sub>) of Cu@CuTCNQ was up to 50.0 mA cm<sup>-2</sup> at -0.8 V vs. RHE, which is 1.8 times higher than that of Cu NPs (27.4 mA cm<sup>-2</sup>, Fig. S17(d)). This is likely because electrons can be easily transferred to the Cu sites from the conductive CuTCNQ substrates [49]. Moreover, the NH<sub>3</sub> yield rate of Cu@CuTCNQ was higher than that of Cu NPs over the entire applied potential range, reaching 144.8 and 233.2 µmol h<sup>-1</sup> cm<sup>-2</sup> at -0.6 and -0.8 V vs. RHE, respectively (Fig. 4(d)). The NRA electrochemical performance of the Cu@CuTCNQ composite was further investigated by three consecutive parallel experiments of potentiostatic electrolysis at -0.6 V vs. RHE (Fig. S18). The results show that the three parallel experiments had almost the same current density, NH3 FE, and yield rate, further confirming the excellent catalytic performance for NRA.

Blank comparisons and isotope labelling experiments were conducted to demonstrate that the detected NH<sub>3</sub> was the result of the reduction of NO3<sup>-</sup>. The reconstituted Cu@CuTCNQ was electrolyzed at -0.6 V vs. RHE for 1 h in 0.1 mol L-1 KOH solution without  $NO_3^-$  (Fig. S19(a)). After electrolysis, the solution was stained with an indophenol blue indicator, which showed a color similar to that of the blank KOH solution (Fig. S19(b)). Further quantitative analysis by UV-vis spectrophotometry showed that in the NO3<sup>-</sup>-free KOH solution, the generated NH3 was hardly detected (Figs. S19(c) and (d)), excluding the possible effects of TCNQ. After adding 14NO3<sup>-</sup> and 15NO3<sup>-</sup> as reactants in a 0.1 mol L-1 KOH solution for the electrolytic reaction, the NMR spectra (Fig. S20) showed the <sup>14</sup>NH<sub>4</sub><sup>+</sup> triple and typical <sup>15</sup>NH<sub>4</sub><sup>+</sup> double peaks with coupling constants of 52.0 and 73.1 Hz, respectively [50]. These results verify that the NH<sub>3</sub> produced was derived from the electrochemical reduction of NO3-. Moreover, based on three independent electrolysis experiments, the average FE and yield rate of the NH3 produced from Cu@CuTCNQ at -0.6 V vs. RHE, determined by 1H NMR spectroscopy, were 95.9% and 144.2 µmol h<sup>-1</sup> cm<sup>-2</sup>, respectively, which were consistent with the results quantified by UV-vis spectrophotometry. <sup>15</sup>N-labeled NO<sub>3</sub><sup>-</sup> was used as a reactant to further study the accumulation of NH3 at different reaction times (Fig. 4(e)). The <sup>1</sup>H NMR spectrum showed only two signals for 15NH4+, and the peak intensity increased with increasing electrolysis time, further confirming that the generated NH<sub>3</sub> originated from the electrochemical NO3<sup>-</sup> reduction and accumulated continuously. The stability of Cu@CuTCNQ was investigated by performing a continuous NO3<sup>-</sup> electrolysis reaction at -0.6 V vs. RHE for 10 h (Fig. 4(f)). The Cu@CuTCNQ catalyst still showed excellent catalytic performance, with a high total NH<sub>3</sub> FE of 84.84% and yield rate of 133.0 µmol h<sup>-1</sup> cm<sup>-2</sup>. SEM characterization showed that the morphology of the Cu@CuTCNQ composite did not change after long-term stability measurements. XRD revealed that the diffraction peaks attributed to CuTCNQ and metallic Cu still existed, highlighting the excellent catalytic stability of the Cu@CuTCNQ composite (Fig. S21). The advantages of the Cu@CuTCNQ catalyst for NRA were further highlighted by comparison with other reported catalysts (Table S2).

The structural evolution and stability of CuTCNQ during NRA were monitored by *in situ* Raman spectroscopy with laser excitation at 633 nm (Fig. S22). The corresponding spectra of CuTCNQ loaded on a glassy carbon electrode, collected at the open-circuit voltage (OCV) and other applied potentials, are shown in Fig. 5. Neutral TCNQ crystals display Raman peaks at 1204, 1450, 1598, and 2222 cm<sup>-1</sup>, assigned to C=CH bending, C–CN wing stretching, C=C ring stretching, and C≡N stretching modes, respectively [42]. When TCNQ is reduced to TCNQ<sup>-</sup> to form CuTCNQ, the two characteristic Raman peaks of C–CN wing stretching and C≡N stretching are shifted to lower wavenumbers, 1375 and 2206 cm<sup>-1</sup>, respectively, owing to metal centers and TCNQ charge transfer [51,52]. During LSV testing



**Fig. 5.** (a,b) Raman spectra of TCNQ and CuTCNQ at open-circuit voltage (OCV) and 0.25 V vs. RHE, respectively. (c,d) Potential-dependent *in situ* Raman spectra of CuTCNQ in 0.1 mol L<sup>-1</sup> KOH solution containing 0.1 mol L<sup>-1</sup> NO<sub>3</sub><sup>-</sup>.

of CuTCNQ, the Raman signal intensity of CuTCNQ under OCV conditions was significantly enhanced when the potential was swept to 0.25 V vs. RHE. This enhancement can be attributed to the electrochemical reduction of the Cu+ ions in CuTCNQ into nanostructured Cu. The resulting nanostructured Cu acts as an active substrate to realize the surface enhanced Raman scattering (SERS) effect (Figs. 5(a) and 5(b)) [53-57]. In addition, the reductive exfoliation of the Cu-N4 node in CuTCNQ was accompanied by an increase in the vibrational energy of the C-CN wing stretching, resulting in a blue shift of the peak to 1389 cm<sup>-1</sup>. The shift in the C-CN wing stretching mode confirms the electronic interaction between the CuTCNQ substrate and derived Cu. This interaction contributes to the higher NO3reduction activity of Cu@CuTCNQ compared to that of the Cu NPs [58]. Although the peak intensity of CuTCNQ weakened to a certain extent as the potential was further negatively scanned between 0.25 and -0.65 V vs. RHE, it did not disappear completely, indicating that the CuTCNQ structure still exists even after the electroreduction reconstruction (Figs. 5(c) and 5(d)). Additionally, the phase evolution of CuTCNQ during the reconstruction process at -0.6 V vs. RHE was further characterized by in situ Raman spectroscopy (Fig. S23). The Raman peak intensity of the CuTCNQ complex (e.g., C-CN wing stretching mode at 1389 cm<sup>-1</sup>) decreased and then remained unchanged during the 2 h reconstruction process under working conditions, indicating a structural change of the material along with the preservation of CuTCNQ after reconstitution. The *in situ* Raman measurements agreed with the characterization results discussed above and further confirmed that the stable Cu@CuTCNQ composites were responsible for the highly selective NRA.

Furthermore, online DEMS was performed to capture the volatile molecular intermediates and products produced during the NRA (Fig. 6(a)). The mass-to-charge ratio (m/z) signals of 30 and 46 attributed to NO and NO<sub>2</sub> were detected in three subsequent electrolysis at a constant potential of -0.6 V vs. RHE, indicating the presence of crucial NO\* and NO<sub>2</sub>\* reaction intermediates over Cu@CuTCNQ [59]. Furthermore, a relative signal assigned to NH<sub>3</sub> appeared at m/z = 17, further confirming the production of ammonia.

The above-mentioned phase analysis combined with catalytic performance studies has shown that Cu is the active phase for the  $NO_3^-$  reduction reaction, and abundant Cu vacancy defects on the Cu surface are more conducive to improving  $NH_3$  selectivity. Based on the characterization of Cu@CuTCNQ, DFT calculations were performed to further elucidate the enhanced catalytic performance of vacancy-defect-rich Cu (V<sub>Cu</sub>-Cu). Based on the constructed structural model (Fig. S24), the charge den-



**Fig. 6.** (a) DEMS measurement of NRA over Cu@CuTCNQ. (b) Optimized charge density difference between perfectly crystallized Cu and  $V_{Cu}$ -Cu after adsorbing NO<sub>3</sub><sup>-</sup>. Cyan and yellow regions indicate the depletion and accumulation of the electron density, respectively. (c) Gibbs free-energy diagram of NRA on Cu and  $V_{Cu}$ -Cu. U = 0.0 V vs. RHE. The inset is the optimized structure models of NRA intermediates adsorbed on  $V_{Cu}$ -Cu. (d) Schematic illustration of the NRA pathway on vacancy defect-rich Cu (111) surface. (e) Free energy of H<sub>2</sub> formation over Cu and  $V_{Cu}$ -Cu. Blue, red, white, and pink spheres represent Cu, O, N, and H atoms, respectively.

sity differences between perfectly crystallized Cu and V<sub>Cu</sub>-Cu after NO3<sup>-</sup> adsorption are plotted in Figs. 6(b) and S25. Compared to NO3<sup>-</sup> adsorbed on the Cu surface in the side-on mode through two O atoms in a chelating O,O-bidentate configuration, the adsorption of NO3<sup>-</sup> on V<sub>Cu</sub>-Cu occurs via the bonding of three O atoms to the Cu atom near the vacancy defect. Moreover, the electron cloud between V<sub>Cu</sub>-Cu and NO<sub>3</sub><sup>-</sup> accumulates more than that on Cu. This increased electron density results in charge-transfer ability, а stronger facilitating the bond-breaking activation of NO<sub>3</sub><sup>-</sup> [60]. However, the remaining CuTCNQ can act as a conductive substrate and play a vital role in the transfer of electrons from the substrate to the active site. Based on DEMS results and previous reports [28,61-63], it can be deduced that the reaction pathway of NRA consists of a series of deoxidation steps (\*NO<sub>3</sub>  $\rightarrow$  \*NO<sub>2</sub>  $\rightarrow$  \*NO  $\rightarrow$  \*N) followed by a series of hydrogenation steps (\*N  $\rightarrow$  \*NH  $\rightarrow$  \*NH<sub>2</sub>  $\rightarrow$  \*NH<sub>3</sub>) at the elemental level. The optimized structures of the intermediates adsorbed on the V<sub>Cu</sub>-Cu and Cu surfaces are shown in Figs. 6(c) and S26, respectively, and the corresponding Gibbs free energy ( $\Delta G$ ) diagrams were calculated for different catalyst surfaces. For perfectly crystallized Cu, the initial NO<sub>3</sub><sup>-</sup> adsorption is an energy-consuming step requiring a  $\Delta G$  of 0.22 eV. After NO<sub>3</sub><sup>-</sup> adsorption, the NRA process is generally exothermic until NH<sub>3</sub> desorption. Although the energy barrier for NH<sub>3</sub> desorption ( $\Delta G = 0.28 \text{ eV}$ ) is higher than that for NO<sub>3</sub><sup>-</sup> adsorption over the Cu surface, NH<sub>3</sub> is readily desorbed from the adsorption sites under practical reaction conditions because of its high solubility in aqueous solutions [64,65]. Furthermore, as the desorption of NH<sub>3</sub> is not an electrochemical step, the PDS in the NRA process over the Cu surface is considered to be NO3<sup>-</sup> adsorption. In contrast, when Cu vacancy defects are introduced into the Cu surface to form  $V_{Cu}$ -Cu, the initial step of NO<sub>3</sub><sup>-</sup> adsorption exhibits a thermodynamically downhill trend with a  $\Delta G$  value of -0.64 eV. This indicates a significant enhancement in the adsorption of  $NO_3^-$  on the V<sub>Cu</sub>-Cu surface, favoring the activation of NO<sub>3</sub><sup>-</sup>. Moreover, throughout the progress of the NRA process,  $\Delta G$  remains negative for all electrochemical steps. This suggests that deoxidation and hydrogenation processes are thermodynamically favorable on the surface of V<sub>Cu</sub>-Cu. A schematic of the NRA pathway on V<sub>Cu</sub>-Cu is shown in Fig. 6(d). The free energy of H\* adsorption on V<sub>Cu</sub>-Cu ( $\Delta G_{H^*}$ = -0.13 eV) is more negative than that on the Cu surface ( $\Delta G_{H^*} = -0.09$  eV), which means V<sub>Cu</sub>-Cu surface is advantageous for the suppression of HER (Fig. 6(e)) [66]. Owing to the improved NO<sub>3</sub><sup>-</sup> adsorption and hydrogenation, as well as the suppression of the competing HER, V<sub>Cu</sub>-Cu exhibited outstanding NO<sub>3</sub><sup>-</sup> reduction activity and NH<sub>3</sub> selectivity, which is in agreement with the experimental results.

#### 4. Conclusions

We developed a highly efficient Cu@CuTCNQ composite catalyst with rich Cu vacancy defects for NRA using a facile electrochemical reconstruction method. The morphology and structural evolution of the Cu@CuTCNQ catalyst during the reconstruction process were determined by *ex situ* SEM combined with *in situ* electrochemical Raman spectroscopy. Owing to the synergistic effect of accelerated charge transfer from the CuTCNQ substrate to the Cu sites and surface vacancy defects, the Cu@CuTCNQ catalyst exhibited superior NRA performance with a maximum FE and productivity of 96.4% and 144.8 µmol  $h^{-1}$  cm<sup>-2</sup>, respectively, at -0.6 V vs. RHE. The Cu@CuTCNQ catalyst outperforms its Cu NP counterparts and most Cu-based catalysts. Furthermore, Cu@CuTCNQ exhibited satisfactory stability during long-term durability experiments. DFT calculations indicated that the introduction of vacancy defects on the Cu surface facilitated NO<sub>3</sub><sup>--</sup> adsorption and hydrogenation while inhibiting the competing HER, which accounted for the enhanced NRA performance. This study highlights the importance of constructing efficient NRA catalysts through *in situ* electrochemical reconstruction strategies and provides fundamental insights into the role of the metal vacancy activity in catalysis.

## **Conflicts of Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## **Electronic supporting information**

Supporting information is available in the online version of this article.

## References

- [1] H. Xu, Y. Ma, J. Chen, W.-X. Zhang, J. Yang, Chem. Soc. Rev., 2022, 51, 2710–2758.
- [2] X. Zhang, Y. Wang, C. Liu, Y. Yu, S. Lu, B. Zhang, *Chem. Eng. J.*, **2021**, 403, 126269.
- [3] P. H. van Langevelde, I. Katsounaros, M. T. M. Koper, *Joule*, 2021, 5, 290–294.
- [4] J. Li, Y. Xiao, F. Shui, M. Yi, Z. Zhang, X. Liu, L. Zhang, Z. You, R. Yang, S. Yang, B. Li, X.-H. Bu, *Chin. J. Chem.*, **2022**, 40, 2445–2450.
- [5] Y. Zeng, C. Priest, G. Wang, G. Wu, Small Methods, 2020, 4, 2000672.
- [6] Y. Wang, C. Wang, M. Li, Y. Yu, B. Zhang, Chem. Soc. Rev., 2021, 50, 6720–6733.
- [7] J. Xu, H. Yan, Z. Jin, C.-J. Jia, Chin. J. Chem., 2019, 37, 364–372.
- [8] H. Fang, D. Liu, Y. Luo, Y. Zhou, S. Liang, X. Wang, B. Lin, L. Jiang, ACS Catal., 2022, 12, 3938–3954.
- [9] Y. Luo, S. Liang, X. Wang, B. Lin, C. Chen, L. Jiang, Chin. J. Chem., 2022, 40, 953–964.
- [10] G. Qing, R. Ghazfar, S. T. Jackowski, F. Habibzadeh, M. M. Ashtiani, C.-P. Chen, M. R. Smith, III, T. W. Hamann, *Chem. Rev.*, **2020**, 120, 5437–5516.
- [11] G. Soloveichik, *Nat. Catal.*, **2019**, 2, 377–380.
- [12] W. Liao, H.-X. Liu, L. Qi, S. Liang, Y. Luo, F. Liu, X. Wang, C.-R. Chang, J. Zhang, L. Jiang, *Cell Rep. Phys. Sci.*, **2021**, 2, 100557.
- [13] W. Liao, L. Qi, Y. Wang, J. Qin, G. Liu, S. Liang, H. He, L. Jiang, Adv. Funct. Mater., 2021, 31, 2009151.
- [14] Z.-Y. Wu, M. Karamad, X. Yong, Q. Huang, D. A. Cullen, P. Zhu, C. Xia, Q. Xiao, M. Shakouri, F.-Y. Chen, J. Y. Kim, Y. Xia, K. Heck, Y. Hu, M. S. Wong, Q. Li, I. Gates, S. Siahrostami, H. Wang, *Nat. Commun.*, 2021, 12, 2870.
- [15] G.-F. Chen, Y. Yuan, H. Jiang, S.-Y. Ren, L.-X. Ding, L. Ma, T. Wu, J. Lu,

## **Graphical Abstract**

Chin. J. Catal., 2023, 50: 324–333 doi: 10.1016/S1872-2067(23)64454-7

Defect-rich Cu@CuTCNQ composites for enhanced electrocatalytic nitrate reduction to ammonia

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Cu@CuTCNQ composites with abundant Cu vacancy defects derived from conductive CuTCNQ *via in situ* electrochemical reconstruction exhibit enhanced activity and selectivity in the electrocatalytic reduction of nitrate to ammonia.

H. Wang, Nat. Energy, 2020, 5, 605-613.

- [16] T. Hu, C. Wang, M. Wang, C. M. Li, C. Guo, ACS Catal., 2021, 11, 14417–14427.
- [17] J. Li, J. Gao, T. Feng, H. Zhang, D. Liu, C. Zhang, S. Huang, C. Wang, F. Du, C. Li, C. Guo, *J. Power Sources*, **2021**, 511, 230463.
- [18] Z. Song, Y. Liu, Y. Zhong, Q. Guo, J. Zeng, Z. Geng, Adv. Mater., 2022, 34, 2204306.
- [19] D. Reyter, D. Bélanger, L. Roue, *Electrochim. Acta*, **2008**, 53, 5977–5984.
- [20] X. Fu, X. Zhao, X. Hu, K. He, Y. Yu, T. Li, Q. Tu, X. Qian, Q. Yue, M. R. Wasielewski, Y. Kang, *Appl. Mater. Today*, **2020**, 19, 100620.
- [21] Y. Wang, W. Zhou, R. Jia, Y. Yu, B. Zhang, Angew. Chem. Int. Ed., 2020, 59, 5350–5354.
- [22] W. He, J. Zhang, S. Dieckhöfer, S. Varhade, A. C. Brix, A. Lielpetere, S. Seisel, J. R. C. Junqueira, W. Schuhmann, *Nat. Commun.*, **2022**, 13, 1129.
- [23] H. Yin, Z. Chen, S. Xiong, J. Chen, C. Wang, R. Wang, Y. Kuwahara, J. Luo, H. Yamashita, Y. Peng, J. Li, *Chem Catal.*, **2021**, 1, 1088–1103.
- [24] W.-J. Sun, H.-Q. Ji, L.-X. Li, H.-Y. Zhang, Z.-K. Wang, J.-H. He, J.-M. Lu, Angew. Chem. Int. Ed., 2021, 60, 22933–22939.
- [25] J. Zhao, L. Liu, Y. Yang, D. Liu, X. Peng, S. Liang, L. Jiang, ACS Sustainable Chem. Eng., 2023, 11, 2468–2475.
- [26] Q. Xue, Z. Wang, Y. Ding, F. Li, Y. Chen, Chin. J. Catal., 2023, 45, 6–16.
- [27] Q. Lei, L. Huang, J. Yin, B. Davaasuren, Y. Yuan, X. Dong, Z.-P. Wu, X. Wang, K. X. Yao, X. Lu, Y. Han, *Nat. Commun.*, **2022**, 13, 4857.
- [28] Q. Hu, Y. Qin, X. Wang, Z. Wang, X. Huang, H. Zheng, K. Gao, H. Yang, P. Zhang, M. Shao, C. He, *Energy Environ. Sci.*, **2021**, 14, 4989–4997.
- [29] W. Wang, J. Duan, Y. Liu, T. Zhai, Adv. Mater., 2022, 34, 2110699.
- [30] Y. Jia, K. Jiang, H. Wang, X. Yao, *Chem*, **2019**, 5, 1371–1397.
- [31] J. Sun, H. Xue, N. Guo, T. Song, Y.-R. Hao, J. Sun, J. Zhang, Q. Wang, Angew. Chem. Int. Ed., 2021, 60, 19435–19441.
- [32] H. Yu, T. Zhou, Z. Wang, Y. Xu, X. Li, L. Wang, H. Wang, Angew. Chem. Int. Ed., 2021, 60, 12027–12031.
- [33] W. Liao, K. Xie, L. Liu, X. Wang, Y. Luo, S. Liang, F. Liu, L. Jiang, J. Energy Chem., 2021, 62, 359–366.
- [34] N. Guo, H. Xue, A. Bao, Z. Wang, J. Sun, T. Song, X. Ge, W. Zhang, K. Huang, F. He, Q. Wang, *Angew. Chem. Int. Ed.*, **2020**, 59, 13778–13784.
- [35] Z. Wang, L. Zhang, T. U. Schülli, Y. Bai, S. A. Monny, A. Du, L. Wang, Angew. Chem. Int. Ed., 2019, 58, 17604–17609.

- [36] Y. Zheng, J. Li, D. Ji, H. Dong, L. Li, H. Fuchs, W. Hu, Small, 2021, 17, 2004143.
- [37] X. Huang, D. Wang, S. Yan, P. An, J. Han, Z. Guo, X. Li, Z. Chen, L. Chang, S. Lu, Z. Tang, *Nano Res.*, **2022**, 15, 7910–7916.
- [38] Y. Huang, C. Fang, R. Zeng, Y. Liu, W. Zhang, Y. Wang, Q. Liu, Y. Huang, *ChemSusChem*, **2017**, 10, 4704–4708.
- [39] L. Dai, Q. Qin, P. Wang, X. Zhao, C. Hu, P. Liu, R. Qin, M. Chen, D. Ou, C. Xu, S. Mo, B. Wu, G. Fu, P. Zhang, N. Zheng, *Sci. Adv.*, **2017**, 3, e1701069.
- [40] C. Fang, Y. Huang, L. Yuan, Y. Liu, W. Chen, Y. Huang, K. Chen, J. Han, Q. Liu, Y. Huang, *Angew. Chem. Int. Ed.*, **2017**, 56, 6793–6797.
- [41] J. Ma, E. Zhou, C. Fan, B. Wu, C. Li, Z.-H. Lu, J. Li, *Chem. Commun.*, 2018, 54, 5578–5581.
- [42] M. Mahajan, S. K. Bhargava, A. P. O'Mullane, *RSC Adv.*, **2013**, 3, 4440–4446.
- [43] R. A. Heintz, H. Zhao, X. Ouyang, G. Grandinetti, J. Cowen, K. R. Dunbar, *Inorg. Chem.*, **1999**, 38, 144–156.
- [44] S. Hu, W. Xiao, W. Yang, J. Yang, Y. Fang, J. Xiong, Z. Luo, H. Deng, Y. Guo, L. Zhang, J. Ding, ACS Appl. Mater. Interfaces, 2018, 10, 17167–17174.
- [45] L. B. Zasada, L. Guio, A. A. Kamin, D. Dhakal, M. Monahan, G. T. Seidler, C. K. Luscombe, D. J. Xiao, J. Am. Chem. Soc., 2022, 144, 4515–4521.
- [46] S. Li, H. Duan, J. Yu, C. Qiu, R. Yu, Y. Chen, Y. Fang, X. Cai, S. Yang, ACS Catal., 2022, 12, 9074–9082.
- [47] T. Ren, K. Ren, M. Wang, M. Liu, Z. Wang, H. Wang, X. Li, L. Wang, Y. Xu, *Chem. Eng. J.*, **2021**, 426, 130759.
- [48] F.-Y. Chen, Z.-Y. Wu, S. Gupta, D. J. Rivera, S. V. Lambeets, S. Pecaut, J. Y. T. Kim, P. Zhu, Y. Z. Finfrock, D. M. Meira, G. King, G. Gao, W. Xu, D. A. Cullen, H. Zhou, Y. Han, D. E. Perea, C. L. Muhich, H. Wang, *Nat. Nanotechnol.*, **2022**, 17, 759–767.
- [49] J.-D. Yi, R. Xie, Z.-L. Xie, G.-L. Chai, T.-F. Liu, R.-P. Chen, Y.-B. Huang, R. Cao, Angew. Chem. Int. Ed., 2020, 59, 23641–23648.
- [50] J. Li, Y. Zhang, C. Liu, L. Zheng, E. Petit, K. Qi, Y. Zhang, H. Wu, W. Wang, A. Tiberj, X. Wang, M. Chhowalla, L. Lajaunie, R. Yu, D. Voiry, *Adv. Funct. Mater.*, **2022**, 32, 2108316.
- [51] C. Zhao, D. R. MacFarlane, A. M. Bond, J. Am. Chem. Soc., 2009, 131, 16195–16205.
- [52] A. Pearson, A. P. O'Mullane, V. Bansal, S. K. Bhargava, *Inorg. Chem.*, 2011, 50, 1705–1712.
- [53] J. F. Li, Y. F. Huang, Y. Ding, Z. L. Yang, S. B. Li, X. S. Zhou, F. R. Fan, W. Zhang, Z. Y. Zhou, D. Y. Wu, B. Ren, Z. L. Wang, Z. Q. Tian, *Na*-



ture, 2010, 464, 392-395.

- [54] Q.-F. He, Y.-J. Zhang, Z.-L. Yang, J.-C. Dong, X.-M. Lin, J.-F. Li, *Chin. J. Chem.*, **2023**, 41, 355–369.
- [55] K. S. Shin, H. S. Lee, S. W. Joo, K. Kim, J. Phys. Chem. C, 2007, 111, 15223–15227.
- [56] J. S. Gao, Z. Q. Tian, Chem. Phys. Lett., 1996, 262, 151–154.
- [57] L.-Y. Chen, J.-S. Yu, T. Fujita, M.-W. Chen, Adv. Funct. Mater., 2009, 19, 1221–1226.
- [58] F. Zhao, B. Wen, W. Niu, Z. Chen, C. Yan, A. Selloni, C. G. Tully, X. Yang, B. E. Koel, J. Am. Chem. Soc., 2021, 143, 15616–15623.
- [59] W. Wen, P. Yan, W. Sun, Y. Zhou, X.-Y. Yu, Adv. Funct. Mater., 2022, 33, 2212236.
- [60] S. Garcia-Segura, M. Lanzarini-Lopes, K. Hristovski, P. Westerhoff,

Appl. Catal. B, 2018, 236, 546-568.

- [61] Y. Wang, A. Xu, Z. Wang, L. Huang, J. Li, F. Li, J. Wicks, M. Luo, D.-H. Nam, C.-S. Tan, Y. Ding, J. Wu, Y. Lum, C.-T. Dinh, D. Sinton, G. Zheng, E. H. Sargent, *J. Am. Chem. Soc.*, **2020**, 142, 5702–5708.
- [62] H. Jing, J. Long, H. Li, X. Fu, J. Xiao, Chin. J. Catal., 2023, 48, 205–213.
- [63] Y. Gao, H. Zhuo, Y. Cao, X. Sun, G. Zhuang, S. Deng, X. Zhong, Z. Wei, J. Wang, *Chin. J. Catal.*, **2019**, 40, 152–159.
- [64] Z. Meng, J.-X. Yao, C.-N. Sun, X. Kang, R. Gao, H.-R. Li, B. Bi, Y.-F. Zhu, J.-M. Yan, Q. Jiang, *Adv. Energy Mater.*, **2022**, 12, 2202105.
- [65] H.-J. Chun, V. Apaja, A. Clayborne, K. Honkala, J. Greeley, ACS Catal., 2017, 7, 3869–3882.
- [66] X. Zou, Y. Zhang, Chem. Soc. Rev., 2015, 44, 5148–5180.

## 富含缺陷的Cu@CuTCNQ复合材料增强电催化硝酸盐还原成氨

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摘要:将硝酸盐(NO<sub>3</sub><sup>¬</sup>)电化学转化为化学原料和燃料氨(NH<sub>3</sub>),有助于可持续地缓解当前严峻的能源和环境危机.然而,电 催化NO<sub>3</sub><sup>¬</sup>还原成NH<sub>3</sub>(NRA)涉及一个缓慢的八电子转移过程,并与水系中的析氢反应(HER)相竞争,这给开发高选择性的 NRA催化剂带来巨大挑战.铜基催化剂是最有应用前景的非贵金属催化剂之一,被广泛用于电化学NO<sub>3</sub><sup>¬</sup>还原研究.然而, 块体铜通常表现出较低的NH<sub>3</sub>选择性且伴随HER竞争反应.近年来,原位表征技术的快速发展使人们能够观察到电解过程 中催化剂的结构演变,并验证原位生成的新的高活性相和局部结构(如应变、空位和晶面)在触发高效催化反应中的作用. 研究表明,缺陷位点不仅表现出独特的电子特性,而且可以调节相邻原子的电子结构,通过形成新的协同配位结构,来增强 化学吸附和改变中间体能垒从而达到最佳性能,已被广泛应用于氧析出、氧还原和二氧化碳还原等电催化反应中.因此, 通过结构演化构建富含铜空位缺陷的催化剂,有望提高NRA的活性和选择性.然而,金属表面缺陷工程对电催化反应的影 响研究较少,相关反应机理仍不清楚.因此,阐明空位缺陷对NRA的影响和反应机理对于开发高效NRA催化剂具有重要的 指导作用.

本文通过简单的原位电化学重构方法构建了一种高效的富含铜空位缺陷的铜@四氰基对苯醌二甲烷铜 (Cu@CuTCNQ)复合催化剂,用于常温常压NRA反应.X射线衍射精修结果联合X射线吸收光谱表征表明,成功合成了 CuTCNQ络合物,其中单分散的金属离子Cu的氧化态为+1价,与N元素配位成键.采用非原位扫描电子显微镜结合原位电 化学拉曼光谱研究了NRA过程中CuTCNQ的形貌和结构演变,C-CN拉曼峰发生蓝移表明从CuTCNQ基底到衍生的Cu位点 间的电荷转移作用加强.高分辨透射电子显微镜结合电子顺磁共振表征结果表明,衍生的Cu位点表面存在丰富的Cu空位 缺陷.丰富的Cu空位缺陷和优化的电荷转移特性使催化剂性能得以提升,在含有0.1 mol L<sup>-1</sup> NO<sub>3</sub><sup>--</sup> mo.1 mol L<sup>-1</sup> KOH溶液 中,Cu@CuTCNQ催化剂在-0.6 V vs. RHE还原电位下NRA反应表现出96.4%法拉第效率和144.8 µmol h<sup>-1</sup> cm<sup>-2</sup>的氨产率,优 于结晶性良好的Cu纳米颗粒和大多数Cu基催化剂.利用在线微分电化学质谱对NRA过程的重要中间体NO\*和NO<sub>2</sub>\*进行 检测,并联合理论计算推测反应途径.结果表明,Cu空位的引入改变了Cu表面的电荷分布,增强了Cu活性位点对NO<sub>3</sub><sup>--</sup> mov 附,降低了电势决速步反应能垒,从而使得NRA的脱氧和加氢过程在热力学上更有利.同时,富含Cu空位缺陷的表面有利 于抑制析氢竞争反应,二者共同增强了NRA的活性和选择性.综上,本文突出了通过原位电化学重构策略构建高效NRA催 化剂的重要性,并提供了对金属空位-活性依赖性关系的基本理解.

关键词: 硝酸盐还原; 氨合成; 铜空位; 电催化; 电化学重构

收稿日期: 2023-02-28. 接受日期: 2023-05-15. 上网时间: 2023-07-25.

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基金来源:国家重点研发计划(2021YFB4000402);国家自然科学基金(52071311,52273277,52072362,21905269);吉林省科技发展计划基金项目(20200201079JC,20220201112GX);中科院青年创新促进会(2021223);国家自然科学基金优秀青年科学基金项目(海外).