Boosting Electrocatalytic Nitrate-to-Ammonia Conversion via Plasma Enhanced CuCo Alloy–Substrate Interaction

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was derived from the regulation of Co to weaken the strong adsorption capacity of Cu and the shift of the d-band center to lower the energy barrier, while Ar-plasma modification promoted the formation of *NO to boost nitrate conversion.

KEYWORDS: ammonia synthesis, nonthermal plasma, nitrate reduction, CuCo alloy electrocatalyst, DFT calculation

INTRODUCTION

Ammonia (NH₃) is one of the essential chemicals and base feedstocks, which is industrially produced mainly through the Haber-Bosch process (HBP) via the reaction between N_2 and H_2 (N₂ + 3H₂ \rightarrow 2NH₃). With gray H_2 from catalytic steam methane reforming as the precursor, HBP consumed 3-5% of the world's natural gas supply and 1-2% of the global energy, emitting more than 300 million metric tons of CO₂ annually. The huge capital investment of HBP related to sophisticated infrastructures and harsh operating conditions (450-500 °C, 20-30 MPa) further hampers its deployment in developing countries or remote areas.¹⁻⁴ Therefore, environmentally benign alternatives are of interest considering the promises of carbon neutrality and decentralized NH₃ production. Among these, the electrocatalytic N₂ reduction reaction (ENRR) is considered one of the most promising technologies to harvest NH₃, benefiting from mild reaction conditions, modular equipment, and effective compatibility with intermittent renewables.⁵⁻⁹ Nevertheless, the extremely low selectivity and NH₃ yield rate limit commercial development and industrial advancement significantly. For instance, the general faradaic efficiency (FE) of conventional ENRR is typically below 15%, and the yield rate of NH₃ is far lower than the target set by the U.S. Department of Energy (10^{-4} mol) cm⁻² h⁻¹).^{10,11} Moreover, theoretical calculations for common transition-metal catalysts in ENRR further illustrate the

density functional theory calculations, the high activity of the CuCo alloy

dilemma of simultaneously realizing high activity and selectivity, based on the scaling relations of the adsorption energies of intermediates. 12

Compared to the high bonding energy of N₂ (N \equiv N, 948 kJ/mol), nitrate has inherent advantages of high aqueous solubility and easy activation of the N \equiv O bond (204 kJ/mol), and was recently proposed as a promising nitrogen source with a higher reaction rate and selectivity for NH₃ production.^{13–15} Currently, nitrate is mainly produced by the Ostwald process via the oxidation of NH₃, while its overuse in various industrial and agricultural activities might induce serious aqueous pollution as well as acid rain, photochemical smog, and soil damage.^{16–19} Compared to directly recycling low-concentration nitrate from industrial wastewater, renewables-driven electrocatalytic nitrate reduction can alleviate the environmental risk load while providing a sustainable NH₃ production and facilitating the synthesis of NH₃-based macromolecular chemicals (e.g., urea and amines).^{20–22} However, the electro-

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catalytic nitrate reduction process is still challenging, due to the sluggish and complex eight-electron reaction process. In addition, the competing hydrogen evolution reaction (HER) occupies the active sites on the surface of the electrocatalysts, thus hampering the adsorption of nitrate on catalysts and decreasing the targeted selectivity of NH₃. Therefore, the rational design of the electrocatalysts is essential to achieving efficient electrocatalytic nitrate reduction for NH₃ production.²³

Cu-based catalysts have exhibited prominent high activity in nitrate-to-NH3 reactions and were widely investigated with the advantage of nitrate affinity and HER inhibition.²⁴ For instance, Fu et al. applied copper nanosheets as an electrocatalyst, achieving a current density of 10 mA cm⁻² at -0.15 V vs RHE, with the NH₃ formation rate of 390.1 μ g cm⁻² h^{-1.25} To address the prevailing deactivation of Cu-based electrocatalysts due to the strong adsorption of intermediates, various strategies like heteroatoms doping and alloying are proposed.²⁶ Wang et al. reported the enhanced activity of NH₃ synthesis from nitrate on a $\mathrm{Cu}_{50}\mathrm{Ni}_{50}$ alloy compared to pure Cu with nearly unit FE.²⁴ Similarly, cobalt has also demonstrated excellent performance in nitrate/nitrite reduction and was validated to enable tandem conversion of the adsorbed intermediate from nitrate conversion to NH3.27,28 Besides, the energy band and the center of the d-band were posited to move toward the Fermi level by introducing a Co phase into a Cu matrix. Thus, we prepared a CuCo alloy to optimize the electronic structure and improve the proton/electron transfer, enabling efficient nitrate-to-NH₃ conversion.

To further enhance the overall electrocatalyst performance, nonthermal plasma (NTP) technology was used to optimize the electrocatalyst-substrate interface.²⁹⁻³¹ Woo et al. compared the effect of different plasma treatments on the peel strength of Ni from polyimide, with the purpose to improve the adhesive force of polymer with metals.³² Kurihara et al. found that plasma treatment can effectively guarantee the adhesion and long-term reliability of liquid crystalline polyester film.³³ Song et al. revealed that plasma could modify adhesive force between the catalyst particles and the substrate via material growth mode changing.³⁴ Furthermore, it was also assumed strengthening the interaction between the electrocatalyst and substrate via plasma may decrease the contact resistance and decrease the potential drop across the electrocatalytic reaction system.

In this study, CuCo alloy was prepared via facile electrodeposition on an NTP-modified carbon substrate. The effect of various operating parameters (the electrodeposition time, nitrate concentration, potential, Cu/Co ratios, pH, and plasma treatment) were systematically investigated in terms of nitrateto-NH₃ activity. To verify the origin of NH₃, ¹⁵N isotope tracing experiments combined with ¹H nuclear magnetic resonance (NMR) test were performed. Electrochemical evaluation, density functional theory (DFT) calculation, and in situ Fourier Transform infrared (FTIR) spectroscopy were performed to reveal the effect of Ar-plasma treatment on the electrocatalyst-substrate interaction as well as the performance of nitrate-to-NH₃ conversion. As a result, a high NH₃ yield rate of 5129.29 μ g cm⁻² h⁻¹ was obtained using Cu₃₀Co₇₀ electrocatalyst at -0.47 V vs RHE with Ar-plasma treated carbon substrate, while nearly unity FE was achieved using $Cu_{50}Co_{50}$ electrocatalyst at -0.27 V vs RHE.

EXPERIMENTAL SETUP AND METHOD

Materials Synthesis. All catalysts were prepared via electrodeposition in a typical three-electrode cell with a carbon substrate (1 \times 1 cm²) as the working electrode, a platinum plate as the counter electrode, and a saturated calomel electrode (SCE) as the reference electrode. 0.05 M H₂SO₄ (Aladdin Ltd.) solutions containing 20 mM $CuSO_4 + Co_2SO_4$ (Aladdin Ltd.) were used as the deposition baths. The Cu/Co ratio of the CuCo alloy catalysts was controlled by adjusting the ratio of CuSO₄/Co₂SO₄. Carbon paper (SGL Carbon Corporate) was used as a substrate and current collector. The electrodeposition was conducted at a current density of 200 mA/cm² for 300 s. The as-prepared electrodes of Cu/Co alloy were rinsed by deionized water (18 M Ω) and then dried in an N₂ atmosphere overnight for subsequent electrocatalysis. Herein, the electrocatalyst CuCo alloys were labeled as Cu₈₀Co₂₀, Cu₅₀Co₅₀, and Cu₃₀Co₇₀, according to the Cu/Co ratios in the deposition solutions which were set at 80/20, 50/50, and 30/70, respectively. To enhance the adhesion between the electrocatalyst and carbon substrate, inductively coupled plasma (ICP) was used to treat the pristine substrate using a 13.56 MHz power source (Kmate, Hero). The pressure of the ICP reactor chamber was evacuated to 10 mTorr using a rotary pump (KYKY, RVP-2). Ar (20 mL/min) was introduced into the reactor by a mass flow controller (MFC). The plasma power of the ICP system was set at 300 W, and the treatment time was set at 5 min, followed by a natural cooling process to room temperature.

Material Characterization. The crystal structures of the samples were characterized via X-ray diffraction (XRD) with the D/max-2550 at room temperature. Scanning electron microscopy (SEM) (Hitachi SU-8010) and transmission electron microscopy (TEM) (Hitachi HT-7700) were employed to investigate the morphology of the samples before and after Ar-plasma modification. The surface compositions of the electrocatalysts were analyzed by X-ray photoelectron spectroscopy (XPS) (ESCALAB 220i-XL Thermo) with Al Ka source of 1486.6 eV. Atomic force microscopy (AFM, Dimension Icon, Bruker Nano INC) was used to estimate the roughness change of carbon substrate induced by plasma treatment. Super-resolution infrared imaging was performed by a mid-infrared photothermal (MIP) imaging and spectroscopy platform (mIRage, Photothermal Spectroscopy Corp.), which was used for morphological and compositional characteristics of prepared alloy electrocatalyst (see details in Supplementary Note 1). In situ Fouriertransform infrared spectroscopy (FTIR) was performed using a Nicolet iS50 equipped with a mercury cadmium telluride detector. The reference spectrum was collected at -0.8 V. The spectra were given in absorption units defined as $A = -\log(R/R_0)$, where R and R_0 represent the reflected IR intensities corresponding to the sampleand reference-single beam spectrum, respectively (see details in Supplementary Note 2).

Measurement of NH₃ Synthesis. The activities of prepared electrocatalysts were evaluated in a typical three-electrode system using an H-type electrolytic cell. 50 mL of 1 M KOH solution was used as the electrolyte, while 0.1 M KNO₃ was added as a precursor. The Nafion proton exchange membrane (PEM) was used to separate the two chambers. The platinum plate was used as the counter electrode, Ag/AgCl was used as the reference electrode, and the working electrode was prepared via the aforementioned method with a size of 1 cm × 1 cm. Ar was continuously purged into the electrolyte to eliminate the interference of the background gas, and the potentiostat test method (i-t) was performed for 1 h at each operation condition. All the experiments were repeated to maintain reproducibility.

The NH₃ quantification was spectrophotometrically determined by the indophenol blue method (see details in Supplementary Note 3). To calculate the NH₃ concentration, the concentration-absorbance curve was calibrated using the standard ammonia chloride solution indicated in Figure S1. NH₃ yield rate was calculated via the equation as follows:

$$Y_{\rm NH_2} = c_{\rm NH_2} \times V/t \tag{1}$$



Figure 1. (a) Plasma-enhanced substrate for CuCo-catalyzed NO₃RR mechanism. (b) Effect of Cu/Co ratio on the NH₃ yield rate and FE using the CuCo alloy catalyst at -0.27 V vs RHE. (c) Effect of electrodeposition time on the NH₃ yield rate and FE. (d) Effect of potential on the NH₃ yield rate and FE using the Cu₈₀Co₂₀ catalyst. (e) Effect of pH on the NH₃ yield rate and FE at -0.27 V vs RHE. (f) Effect of nitrate concentration on the NH₃ yield rate and FE at -0.67 V vs RHE.

where Y_{NH_3} was the NH₃ yield rate; C_{NH_3} was the measured NH₃ concentration; V was the volume of electrolyte; t was the reaction time during electrocatalysis.

FE was calculated according to the following equation:

$$FE = \frac{n \times V_{catholyte} \times c_{NH_3} \times F}{i \times t}$$
(2)

where *i* is the total current; *n* represents the number of electron transfers toward the formation of 1 molecule of ammonia, which is 8 for nitrate reduction; $V_{\text{catholyte}}$ is the volume of catholyte (mL); C_{NH_3} represents the concentration of ammonia (M); *F* is the Faraday constant (96485 C mol⁻¹); *t* is the electrolysis time.

To exclude the influence of N-source from the environment, a ¹⁵N isotope labeling experiment was performed combined with ¹H NMR (600 MHz, Agilent Technologies) test, which can also validate the accuracy of the indophenol blue method for NH₃ quantification. KNO₃₋¹⁵N (Macklin, >98.5%) was utilized as the nitrogen source, and $^{15}\mathrm{NH_4Cl}$ was utilized to calibrate the standard curve. The $\mathrm{NH_4^+}$ product with KNO3-15N nitrogen source was tested to confirm the source of nitrogen in ammonia by comparison with the ${}^{14}NH_4^+$ peak. Then, calibration was performed by preparing a series of standard $^{15}\mathrm{NH_4^+}$ concentrations (200–1000 ppm) to quantitatively measure ammonia and verify the accuracy of the indophenol blue method. During each test, 40 mL of the solution (after the electrocatalysis process) was extracted to be measured, and the pH was adjusted to 2-3, followed by mixing with 100 ppm of maleic acid as an internal standard. 0.5 mL of the above solution was added to 50 μ L of D₂O for NMR testing.

DFT Calculation. The calculations were calculated in the "Vienna ab initio simulation package" (VASP) within the framework of density functional theory (DFT). Perdew–Burke–Ernzerhof (PBE) exchange-correlation functional was used to calculate the adsorption energies. To simulate the reaction on the surface of the catalyst, the supercell was used with a vacuum layer of 15 Å. Brillouin zone was accomplished by $3 \times 3 \times 1$ Monkhorst–Pack k-point mesh for the systems. The plane-wave was considered with the energy cutoff at 400 eV. The long-range dispersion interaction was described by the DFT-D3 method. The convergence criteria for the total energy and the Hellman-Feynman force are 10^{-5} eV and 0.02 eV Å⁻¹, respectively. Gibbs free energy for the elemental steps was calculated by the following equation:

$$G = E + E_{\rm ZPE} - T\Delta S \tag{3}$$

E, E_{ZPE} , *T*, and S were defined as the DFT total energy, zero-point energy, absolute temperature (298.15 K), and entropy, respectively.

VASPKIT was used to calculate zero-point energy and entropy of the intermediates.

RESULTS AND DISCUSSION

To evaluate the electrocatalytic activity, different pH values, potentials, and Cu/Co ratios were systematically investigated in a typical H-type cell, as demonstrated in Figure 1a. Compared to pure Cu and Co, CuCo alloy exhibited a significant increase of the reaction activity in terms of NH₃ yield rate and FE, regardless of the Cu/Co ratios (Figure 1b). To confirm the optimum electrodeposition time, we adjusted the electrodeposition time from 100 to 500 s. It was observed that NH₃ yield rate and FE increased significantly when the electrodeposition time increased from 100 s (1233.96 μ g cm⁻² h^{-1} , 43.2%) to 300 s (6205.28 µg cm⁻² h^{-1} , 83.0%). However, a further increase of the electrodeposition time will deteriorate the reaction performance, with that NH₃ yield rate and FE decreased to 5092.12 μ g cm⁻² h⁻¹ and 59.2% at 500 s, respectively. (Figure 1c). At -0.27 V vs RHE, the highest NH₃ yield rate of 2793 μ g cm⁻² h⁻¹ was achieved with nearly 100% FE using the Cu₈₀Co₂₀ electrocatalyst. However, Cu₅₀Co₅₀ exhibited inferior activity compared to Cu₃₀Co₇₀ and $Cu_{80}Co_{20}$. When negative shifting the potential from -0.07vs RHE to -0.67 V vs RHE (Figure 1d), the NH₃ yield rate increased almost linearly from 853 μ g cm⁻² h⁻¹ to 6205 μ g cm⁻² h⁻¹. Moreover, CuCo alloy exhibited a relatively high NH_3 yield rate and FE (>80%) for acid (pH = 2) and base environment (pH = 13, 14), while the reaction activity dropped sharply at the neutral electrolyte phosphate buffer saline (PBS) as shown in Figure 1e. The performance of the catalyst was also investigated for different concentrations of nitrate (Figure 1f). The NH₃ yield rate increased monotonically with a higher concentration, from 879.64 μ g cm⁻² h⁻¹ at 2000 ppm to 5129.29 μ g cm⁻² h⁻¹ at 6000 ppm. Considerable FE (~80%) was achieved at nitrate concentrations above 4000 ppm. To investigate the performance of the catalyst at low nitrate concentrations, we carried out the measurement at concentrations close to that of underground water (100, 200, 400, and 800 ppm). Figure S2 exhibited a trend of increasing NH₃ yield rate from 362.85 μ g cm⁻² h⁻¹ at 100 ppm to 783.95 $\mu g \text{ cm}^{-2} \text{ h}^{-1}$ at 800 ppm with higher concentrations.



Figure 2. Contact angle measurement and AFM images of carbon substrate (a) without and (b) with Ar-plasma treatment; (c) comparison of ECSAs using different electrocatalysts (pure Cu, Ar-plasma modified Cu (Cu-NTP), $Cu_{30}Co_{70}$, and Ar-plasma modified $Cu_{30}Co_{70}$ ($Cu_{30}Co_{70}$ -NTP)); (d) LSV curves of nitrate reduction on the different electrocatalysts (pure Cu, Cu-NTP, $Cu_{30}Co_{70}$, and $Cu_{30}Co_{70}$ -NTP) in 0.1 M KNO₃ electrolyte without *iR* compensation.

Compared to \sim 80% FE above 4000 ppm, the FE was greatly suppressed in low concentration environments (22% at 800 ppm, \sim 10% at 100 ppm to 400 ppm). Therefore, the catalyst is more prone to apply in nitrate-enriched wastewater.

By measuring the byproducts, we detected H_2 dominated due to the competitive HER, along with trace amounts of NO₂⁻. It was observed HER was suppressed, and the FE of ammonia was promoted from 48% (-0.27 V vs RHE) to 83% (-0.67 V vs RHE) by increasing the reduction potential, and a slight change of the FE of nitrite was observed with its value fluctuating between 1% and 3%. (Figure S3).³⁵ In addition, the concentrations of the ions in the electrolyte such as ammonia, nitrate, and nitrite were also investigated during the nitrate-to-NH₃ conversion process. It was observed that NH₃ was accumulated monotonically during the reaction combined with the continuous consumption of nitrate ions, while little nitrite was produced, and its concentration was almost unchanged (Figure S4).

During the preparation of the CuCo alloy catalysts, metal shedding was observed (Figure S5), which implied a relatively weak adhesion of the electrocatalyst to carbon. It was assumed the weak CuCo alloy-substrate interaction might cause large contact resistance and increase the voltage drop across the substrate-electrocatalyst interface. Nonthermal plasma, widely employed for modifying the surface characteristics (such as roughness, functional group, and hydrophobicity), was employed to increase the adhesive force between carbon substrate and CuCo alloy.³⁶ By comparing three types of carrier gases (air, Ar, and N₂), electrocatalyst with Ar-plasma modified substrate outperformed the counterparts as shown in Figure S6. Different from the air or N_2 plasma that is normally used to introduce oxygen- or nitrogen-contained radicals and components into the electrocatalyst, Ar-plasma was prone to change the physical roughness and hydrophobicity.

Based on contact angle measurements in Figure 2a,b, the pristine carbon substrate was hydrophobic with the contact

angle of 149.8°, while it turned into hydrophilic with the contact angle of 65.1° after Ar-plasma treatment (300 W) for 5 min. Similarly, the AFM topography images also demonstrated that Ar-plasma treated carbon substrate was much rougher with the occurrence of dense peaks and valleys, compared to the relatively flat surface of the pristine carbon substrate. It was speculated that the plasma modification might remove weak boundaries and introduce undulation on the surface, contributing to the increase of the specific surface area and more anchoring sites. To get insight into the strengthened interaction of the catalyst-substrate surface, we compared the electrochemically active surface area (ECSA) of different electrocatalysts by measuring the double-layer capacitances $(C_{\rm dl})$ in Figure 2c and Figure S7. The Cu₃₀Co₇₀-NTP and pure Cu-NTP substrate indicated a larger C_{dl} of 14.7 mF cm⁻² and 4.87 mF cm $^{-2}$, respectively, compared to counterparts without plasma modification. It was assumed that active species in Arplasma (such as energetic electrons and Ar metastable molecules) will roughen the carbon surface by breaking the chemical bonds via bombardment. Then, the radicals on the surface could rebond to form a cross-linked network structure, enhancing the interaction between the substrate and the catalyst.^{37,38} After Ar-plasma modification, CuCo alloy exhibited an effective and homogeneous adherence to the carbon substrate (Figure S8). On the other hand, optimizing the substrate-catalyst interface via Ar-plasma modification might contribute to a lower resistance (derived from the change of polaron hopping barrier and charge-transfer resistance) and higher surface activity (derived from the change of Gibbs free energy and double-layer capacitance), resulting in better activity for nitrate electro-conversion.³⁹ As shown in Figure S9, electrochemical impedance spectroscopy (EIS) measurements were performed and fitted to an equivalent circuit model, where the semicircle represented the charge transfer resistance (R_{ct}) at the catalyst surface. After the Ar-plasma treatment, the R_{ct} of the electrocatalyst was

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Figure 3. TEM images of (a) pure Cu catalyst and (b) $Cu_{30}Co_{70}$ -NTP. Comparison of XRD patterns of different electrocatalyst deposition on the (c) untreated substrate and (d) the Ar-plasma treated substrate, respectively. The XPS Cu 2p (e) and Co 2p (f) spectra of $Cu_{30}Co_{70}$ -NTP.



Figure 4. Super-resolution IR imaging characterization of $Cu_{30}Co_{70}$ -NTP. (a) Brightfield image. (b) Reflectance image of the area indicated by the white box in (a) with 532 nm laser illumination. (c) Super-resolution IR imaging of the same area by mid-infrared photothermal (MIP) imaging at 1595 cm⁻¹ CuCo band. (d) Overlay of the reflectance and IR image. Scale bars: 50 μ m.

reduced from 24.57 Ω to 18.65 Ω , indicating a significant reduction in the resistance of the electrode–electrolyte interface and the promotion of electron transfer by substrate enhancement. As illustrated in Figure 2d, Cu₃₀Co₇₀-NTP exhibited excellent performance of nitrate reduction with an ultralow onset potential, superior to all other electrocatalysts. Under alkaline conditions, only a potential of 0.1 V was required to reach the current density of 50 mA cm⁻² over Cu₃₀Co₇₀-NTP, while the current density exceeded over 150 mA cm⁻² at -0.2 V vs RHE (Figure 2c).

To get insight into the nitrate-to-NH₃ conversion reaction over CuCo alloy surface, the morphology and structure were characterized. In Figure 3a,b, the SEM and TEM images of pristine Cu and Cu₃₀Co₇₀-NTP were compared. Different from the dendritic morphologies observed from the pure Cu samples, the growth of spherical Cu₃₀Co₇₀ alloy nanoparticles with an average particle size of ~50 nm was observed on the Ar-plasma treated substrate. Based on the TEM image (Figure S10), the aggregation of the ellipsoidal alloy particles was observed while EDS mapping demonstrated the homogeneous distribution of Cu and Co elements over all the structure (Figure S11). A typical lattice spacing of Cu(111) facets was observed with the lattice space of ~0.209 nm, while the typical lattice spaces of ~0.179 and 0.207 nm corresponding to the formation of CuCo(220) and CuCo(111) were observed. In addition, the actual metal loading was measured by inductively coupled plasma-optical emission spectroscopy (ICP-OES), which demonstrated a CuCo loading ratio (Table S1). As shown in Figure 3c,d, XRD characterization demonstrated the existence of CuCo(111) and CuCo(200) peaks consistent with the observation from the TEM images. And the broader diffraction peaks of Cu₃₀Co₇₀-NTP revealed the smaller nanograin sizes generated, which showed better nanocluster dispersion over that without plasma treatment. According to XPS spectra, the coexistence of Cu and Co was observed on the Ar-plasma treated substrate (Figure 3e,f). Co 2p spectra demonstrated a prominent peak at ~797 eV, which was assigned to Co $2p_{1/2}$. The binding energies at ~781 eV should be attributed to the metallic state of $\text{Co}^0 2p_{3/2}$. The Cu 2p spectra of Cu₃₀Co₇₀ alloy featured peaks at ~952 eV and ~932 eV, which corresponded to the Cu $2p_{1/2}$ and Cu $2p_{3/2}$, respectively.⁴⁰⁻⁴² Furthermore, compared with Cu₅₀Co₅₀ and Cu catalysts, Cu₃₀Co₇₀-NTP demonstrated more satellite peaks in the Cu 2p energy spectrum, indicating more of a Cu-Co



Figure 5. (a) The effect of Cu/Co ratio on the NH₃ yield rate and FE at -0.07, -0.27, -0.47, and -0.67 V vs RHE. (b) The effect of potential on the NH₃ yield rate and FE using Cu₃₀Co₇₀ and Cu₃₀Co₇₀-NTP at -0.27 V vs RHE. (c) ¹H NMR spectra of ¹⁵N-NH₄⁺ with different concentrations. (d) Comparison of NH₃ production rate and FE by ultraviolet-visible spectroscopy (UV-vis) method and NMR method. (e) Stability test of Cu₃₀Co₇₀-NTP.

alloy structure in $Cu_{30}Co_{70}$,⁴³ which further unveiled the origin of the catalyst activity.

Then, super-resolution infrared (IR) imaging was applied to reveal the intuitive distribution of active CoCu sites at the submicrometer scale level. It was realized by a mid-infrared photothermal (MIP) microscope with submicrometer spatial resolution and high IR spectral fidelity.44-46 In brief, a submillimeter field-of-view (FOV) brightfield imaging was performed with white light illumination and visible color complementary metal oxide semiconductor (CMOS) detector to reveal the corrugated structures of the catalyst substrate (Figure 4a,b). The region of interest (ROI) of about 240 μ m in width, as indicated by the box, was then selected for spectroscopic IR imaging analysis. CuCo alloy-related peak at 1595 cm⁻¹ was selected for IR imaging, according to previous studies.^{47–49} Prior to MIP imaging, the ROI was confirmed by reflectance imaging of the same probe laser (532 nm, Cobolt Hubner Photonics) (Figure 4c). The images were overlaid for colocalization verification (Figure 4d). Compared to the infocus areas of the reflectance image, the alloy electrocatalysis sites were observed to equally distribute over the substrate. The macro-distribution of CuCo alloy sites also varied in size, ranging from a few hundred nanometers to a few micrometers, indicating a relatively good dispersion of the electrocatalyst over the substrate after the Ar-plasma treatment.

The comparative analysis of nitrate-to-NH₃ activity was investigated in terms of different potentials and Cu/Co ratios, to systematically validate the effect of Ar-plasma modification on the catalyst-substrate interface. As expected, for all Cu/Co ratios, the electrocatalyst with Ar-plasma modification exhibited a dramatic increase in NH₃ yield rate (Figure 5a). For the Cu/Co ratio of 50:50, the NH₃ yield rate increased by 36% after Ar-plasma treatment, accompanied by an increase of the FE from 68.4% to nearly 100%. The NH₃ yield rate had a distinct enhancement regardless of the potential and pH variation, as depicted in Figure 5b and Figure S12. At-0.47 V vs RHE, the NH₃ yield rate increased to 5129.29 μ g cm⁻² h⁻¹ using Ar-plasma treated substrate without the sacrifice of FE. As shown in Table S2, the NH₃ yield rate reported here outperformed most previous nitrate-to-NH3 conversions over various state-of-the-art electrocatalysts.

On the other hand, to verify that nitrate was the sole N source for ammonia harvest, an isotope labeling experiment was performed. No triplet peaks corresponding to ¹⁴N was observed in the solution after electrocatalysis, indicating that nitrate is the only source of nitrogen instead of other contaminants. The yield rate of ¹⁵NH₄⁺ was quantified by ¹H NMR spectra with external standards of maleic acid. The results further confirmed the accuracy of the spectrophoto-



Figure 6. In-situ FTIR spectra of (a) the $Cu_{30}Co_{70}$ and (b) $Cu_{30}Co_{70}$ -NTP via linear scanning in 1 M KOH + 0.1 M KNO₃ at different potentials ($-0.9 \sim -1.2$ V vs Ag/AgCl) and DFT calculations: (c) Free energy diagram with the different reaction pathways on the catalyst surface. (d) The partial density of states (PODS) of $Cu_{30}Co_{70}$, $Cu_{50}Co_{50}$, and $Cu_{80}Co_{20}$ alloy. (e) Crystal orbital Hamilton population (COHP) for catalyst adsorption of NH₃.

metric method using the indophenol blue method (Figure 5c,d).

The long-term stability of the electrocatalyst is also an indicator for evaluating the catalytic performance. A long-term experiment of 10 cycles was performed on $Cu_{30}Co_{70}$ electrocatalyst (Figure 5e), which indicated the current density remained stable together with an almost constant NH₃ yield rate. As shown in Figure S13, SEM and XPS characterization of $Cu_{30}Co_{70}$ electrocatalyst after the long-term reaction (10 h) was performed. For Co_{2p} orbitals, the positions of Co $2p_{3/2}$, Co $2p_{1/2}$ and satellite peaks did not shift, with the peak width and peak height being relatively consistent, which was also verified by the Cu 2p orbital. However, the difference in some satellite peaks was observed in Cu spectra, which might be due to the formation of copper oxides. In addition, no release of metal was observed after the reaction in the electrolyte.

Then, DFT calculation and in situ FTIR spectroscopy were performed to unravel the reaction pathway and the origin of high nitrate-to-NH₃ activity from CuCo alloy and the effect of Ar-plasma treatment. As shown in the FTIR spectra (Figure 6a,b), the negative bands at ~1250 cm⁻¹, corresponding to the intermediates of *NO₂, and H–N–H bend of NH₃ at ~1630 cm⁻¹, were observed during nitrate conversion using Cu₃₀Co₇₀ alloy. With the decrease of potential from –0.9 to –1.2 V vs Ag/AgCl, the shifting of NH₃ bands to large wavenumber was observed, together with the observation of the transformation of NO₂⁻ band to *NO band at ~1350 cm^{-150–5253}. As for the Cu₃₀Co₇₀ alloy with the substrate modified by Ar-plasma, only two obvious bands assigned to NH₃ and NO were observed with the variation of applied potential. Hence, *NO was

assumed as a key intermediate for nitrate conversion and was prone to form after plasma treatment. Considering the different adsorption directions on various adsorption sites, the total energy on the stabilized intermediates over the surface the electrocatalysts was calculated, and the lowest free energy was the most stable configuration of the intermediate (Figure S14). In a typical alkaline (1 M KOH) environment, the reaction process of NH₃ synthesis from nitrate reduction was considered through a series of deoxidation and hydrogenation reactions.

$$NO_{3^-} + 6H_2O + 8e^- \rightarrow NH_3 + 9OH^-$$
(4)

The structural relaxation of CuCo may have occurred because Co was prone to replace Cu atoms of the subsurface dependent on the thermodynamics so that the nitrate ions were more inclined to bond with Cu on the surface. By calculating the intermediate's free energy at each step, the potential catalytic mechanism was revealed. The deoxygenation reaction spontaneously occurs with the CuCo catalysts during the nitrate reduction to NH₃, which corroborated with the observation of more NO species based on in situ FTIR spectra. It can be judged from the energy path in Figure 6c, that the catalytic deoxidation process of Co was significantly weaker than that of Cu, especially in the $*NO_3 \rightarrow *NO_2$ process. However, the catalyst poisoning caused by the adsorption of nitrogen oxides hampered Cu carrying out the subsequent reaction. The CuCo-doped catalysts adjusted the NO adsorption and hydro-desorption capacity. The relatively low activity and selectivity of the $Cu_{80}Co_{20}$ electrocatalyst originated from a higher energy barrier during the hydrogenation process of *NH \rightarrow *NH₂. With the increase of the doping ratio of Co, the performance of Cu₅₀Co₅₀ can be improved to a certain extent attributed to the change of energy barrier, while the performance reaches its peak using Cu₃₀Co₇₀ as an electrocatalyst. It was due to the lowest energy difference (0.775 eV) of the rate-determining step (RDS), resulting in high selectivity and high efficiency of catalyzing nitrate to NH₃.

In Figure 6d, the calculation of partial density of states (PDOS) calculation indicated that Cu₃₀Co₇₀ alloy possessed a higher d-band center near the Fermi level, which was ~1.28 eV higher than that of $Cu_{50}Co_{50}$ alloy, and ~1.66 eV higher than that of the Cu₈₀Co₂₀ alloy, respectively. Hence, it pushed the antibonding orbital higher than the Fermi level, which was conducive to adsorption. Therefore, the Cu₃₀Co₇₀ alloy exhibited a better performance compared to the counterpart electrocatalyst. Cu and Co showed different properties in the last step of ammonia desorption (* $NH_3 \rightarrow NH_3$), so COHP calculations were performed for Cu-N and Co-N in *NH₃. The COHP value of Cu-N (-3.377 eV) was significantly lower than that of Co-N (-2.976 eV), which reflected that Cu benefited from a stronger adsorption capacity for NH₃ adsorbed species (Figure 6e). It was inferred that the doping of Co could improve the overall performance of the catalyst by optimizing the desorption of NH₃.

CONCLUSION

In this study, a highly efficient bimetallic CuCo alloy electrocatalyst was designed for NH₃ production from electrochemical nitrate reduction. It was demonstrated that Ar-plasma modification could boost the activity of the electrocatalyst by enhancing the adhesion force between the CuCo alloy and carbon substrate. Based on the analysis of ECSA and surface characteristics, we demonstrated that the plasma modification of CuCo alloy changed the hydrophobicity of the carbon substrate. By optimizing the potential and Cu/Co ratio, the NH₃ yield rate of 5129.29 μ g cm⁻² h⁻¹ was achieved at -0.47 V (vs RHE) using Cu₃₀Co₇₀ after Arplasma treatment. Furthermore, in situ FTIR spectra confirmed the formation of *NO and intermediate of NO₂⁻ during nitrate conversion, while plasma-modification facilitated the generation of NH₃ and N-related intermediates. The DFT revealed that the activity of Cu₃₀Co₇₀ was due to the lowest energy difference (0.775 eV) in RDS, with a higher d-band center and the stronger desorption capacity of NH₃. Based on this study, we provided an effective strategy to optimize both interfaces of substrate-electrocatalyst and electrocatalystelectrolyte to realize efficient NH₃ synthesis from electrocatalytic nitrate conversion.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acssuschemeng.2c04249.

Standard curves for product measurements; NH3 yield and FE; variation in nitrogen species concentration in solution; ECSA and EIS measurements; XPS and SEM characterization of catalysts; performance comparison; DFT models (PDF)

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Foster, S. L.; Bakovic, S. I. P.; Duda, R. D.; Maheshwari, S.; Milton, R. D.; Minteer, S. D.; Janik, M. J.; Renner, J. N.; Greenlee, L. F. Catalysts for nitrogen reduction to ammonia. *Nat. Catal.* **2018**, *1*, 490–500.

(2) Lee, H. K.; Koh, C. S. L.; Lee, Y. H.; Liu, C.; Phang, I. Y.; Hang, X.; Tsung, C.; Ling, Y. X. Favoring the unfavored: selective electrochemical nitrogen fixation using a reticular chemistry approach. *Sci. Adv.* **2018**, *4*, No. eaar3208.

(3) Kitano, M.; Kanbara, S.; Inoue, Y.; Kuganathan, N.; Sushko, P. V.; Yokoyama, T.; Hara, M.; Hosono, H. Electride support boosts nitrogen dissociation over ruthenium catalyst and shifts the bottleneck in ammonia synthesis. *Nat. Commun.* **2015**, *6*, 6731.

(4) Shipman, M. A.; Symes, M. D. Recent progress towards the electrosynthesis of ammonia from sustainable resources. *Catal. Today.* **2017**, 286, 57–68.

(5) Chen, J. G.; Crooks, R. M.; Seefeldt, L. C.; Bren, K. L.; Bullock, R. M.; Darensbourg, M. Y.; Holland, P. L.; Hoffman, B.; Janik, M. J.; Jones, A. K.; Kanatzidis, M. G.; King, P.; Lancaster, K. M.; Lymar, S. V.; Pfromm, P.; Schneider, W. F.; Schrock, R. R. Beyond fossil fueldriven nitrogen transformations. *Science* **2018**, *360*, 1.

(6) Xu, X.; Tian, X.; Sun, B.; Liang, Z.; Cui, H.; Tian, J.; Shao, M. 1 T-phase molybdenum sulfide nanodots enable efficient electrocatalytic nitrogen fixation under ambient conditions. *Appl. Catal. B Environ.* **2020**, *272*, 118984.

(7) Yang, X.; Sun, S.; Meng, L.; Li, K.; Mukherjee, S.; Chen, X.; Lv, J.; Liang, S.; Zang, H.; Yan, L.; Wu, G. Molecular single iron site catalysts for electrochemical nitrogen fixation under ambient conditions. *Appl. Catal. B Environ.* **2021**, *28*, 119794.

(8) Xiao, L.; Zhu, S.; Liang, Y.; Li, Z.; Wu, S.; Luo, S.; Chang, C.; Cui, Z. Effects of hydrophobic layer on selective electrochemical nitrogen fixation of self-supporting nanoporous Mo_4P_3 catalyst under ambient conditions. *Appl. Catal. B Environ.* **2021**, *286*, 119895.

(9) Shi, Y.; Liu, Y. Vacancy and N dopants facilitated Ti3+ sites activity in 3D Ti3- xC2Ty MXene for electrochemical nitrogen fixation. *Appl. Catal. B Environ.* **2021**, *297*, 120482.

(10) Wang, C.; Gu, L.-L.; Qiu, S.-Y.; Gao, J.; Zhang, Y.-C.; Wang, K.-X.; Zou, J.-J.; Zuo, P.-J.; Zhu, X.-D. Modulating CoFe2O4 nanocube with oxygen vacancy and carbon wrapper towards enhanced electrocatalytic nitrogen reduction to ammonia. *Appl. Catal. B Environ.* **2021**, *297*, 120452.

(11) Martin, A. J.; Perez-Ramirez, J. Heading to distributed electrocatalytic conversion of small abundant molecules into fuels, chemicals, and fertilizers. *Joule* **2019**, *3*, 2602–2621.

(12) Montoya, J. H.; Tsai, C.; Vojvodic, A.; Nørskov, J. K. The challenge of electrochemical ammonia synthesis: a new perspective on the role of nitrogen scaling relations. *ChemSusChem.* **2015**, *8*, 2180–2186.

(13) Cai, J.; Wei, Y.; Cao, A.; Huang, J.; Jiang, Z.; Lu, S.; Zang, S. Electrocatalytic nitrate-to-ammonia conversion with ~ 100% Faradaic efficiency via single-atom alloying. *Appl. Catal., B* 2022, *316*, 121683.
(14) Lu, X.; Yu, J.; Cai, J.; Zhang, Q.; Yang, S.; Gu, L.; Waterhouse, G. I. N.; Zang, S.; Yang, B.; Lu, S. Exclusive nitrate to ammonia

conversion via boron-doped carbon dots induced surface Lewis acid sites. *Cell Rep. Phys. Sci.* **2022**, *3*, 100961.

(15) Lu, X.; Song, H.; Cai, J.; Lu, S. Recent development of electrochemical nitrate reduction to ammonia: A mini review. *Electrochem. Commun.* **2021**, *129*, 107094.

(16) Davidson, E. A.; David, M. B.; Galloway, J. N.; Goodale, C. L.; Haeuber, R.; Harrison, J. A.; Howarth, R. W.; Jaynes, D. B.; Lowrance, R. R.; Thomas, N. B.; Peel, J. L.; Pinder, R. W.; Porter, E.; Snyder, C. S.; Townsend, A. R.; Ward, M. H.Excess Nitrogen in the U.S. Environment: Trends, Risks, and Solutions. *Issues in Ecology*; USGS Publications Warehouse, **2012***1*21–16. http://pubs.er.usgs.gov/ publication/70032270

(17) Duca, M.; Koper, M. T. M. Powering denitrification: the perspectives of electrocatalytic nitrate reduction. *Energy Environ. Sci.* **2012**, *5*, 9726–9742.

(18) Rosca, V.; Duca, M.; de Groot, M. T.; Koper, M. T. M. Nitrogen cycle electrocatalysis. *Chem. Rev.* **2009**, *109*, 2209–2244.

(19) Seraj, S.; Kunal, P.; Li, H.; Henkelman, G.; Humphrey, S. M.; Werth, C. J. PdAu alloy nanoparticle catalysts: effective candidates for nitrite reduction in water. *ACS Catal.* **2017**, *7*, 3268–3276.

(20) Butcher, D. P.; Gewirth, A. A. Nitrate reduction pathways on Cu single crystal surfaces: Effect of oxide and Cl-. *Nano Energy.* **2016**, 29, 457–465.

(21) Pérez-Gallent, E.; Figueiredo, M. C.; Katsounaros, I.; Koper, M. T. M. Electrocatalytic reduction of nitrate on copper single crystals in acidic and alkaline solutions. *Electrochim. Acta* **2017**, *227*, 77–84.

(22) Hawtof, R.; Ghosh, S.; Guarr, E.; Xu, C.; Sankaran, R. M.; Renner, J. N. Catalyst-free, highly selective synthesis of ammonia from nitrogen and water by a plasma electrolytic system. *Sci. Adv.* **2019**, *5*, No. 5778.

(23) Singh, A. R.; Rohr, B. A.; Schwalbe, J. A.; Cargnello, M.; Chan, K.; Jaramillo, T. F.; Chorkendorff, I.; Nørskov, J. K. Electrochemical ammonia synthesis-the selectivity challenge. *ACS Catal.* **2017**, *7*, 706–709.

(24) McEnaney, J. M.; Blair, S. J.; Nielander, A. C.; Schwalbe, J. A.; Koshy, D. M.; Cargnello, M.; Jaramillo, T. F. Electrolyte Engineering for Efficient Electrochemical Nitrate Reduction to Ammonia on a Titanium Electrode. *ACS Sustain. Chem. Eng.* **2020**, *7*, 2672–2681.

(25) Fu, X.; Zhao, X.; Hu, X.; He, K.; Yu, Y.; Li, T.; Tu, Q.; Qian, X.; Yue, Q.; Wasielewski, M. R.; Kang, Y. Alternative route for electrochemical ammonia synthesis by reduction of nitrate on copper nanosheets. *Appl. Mater.* **2020**, *4*, 100620.

(26) He, W.; Zhang, J.; Dieckhofer, S.; Varhade, S.; Brix, A. C.; Lielpetere, A.; Seisel, S.; Junqueira, J. R. C.; Schuhmann, W. Splicing the active phases of copper/cobalt-based catalysts achieves high-rate tandem electroreduction of nitrate to ammonia. *Nat. Commun.* **2022**, *13*, 1129.

(27) Wang, Y.; Xu, A.; Wang, Z.; Huang, L.; Li, J.; Li, F.; Wicks, J.; Luo, M.; Nam, D.; Tan, C.; Ding, Y.; Wu, J.; Lum, Y.; Dinh, C.; Sinton, D.; Zheng, G.; Sargent, E. H. Enhanced Nitrate-to-Ammonia Activity on Copper-Nickel Alloys via Tuning of Intermediate Adsorption. J. Am. Chem. Soc. **2020**, 142, 5702–5708.

(28) Cheng, H.; Huang, Y.; Wang, A.; Wang, X.; Zhang, T. Preparation of Cobalt Nitride from Co–Al Hydrotalcite and its Application in Hydrazine Decomposition. *Top Catal.* **2009**, *52*, 1535–1540.

(29) Wang, R.; Ye, B.; Kong, X.; Xia, Z.; Zhang, Z.; Li, H.; Xie, P. Research Progress of Low Temperature Plasma Surface Strengthening Technology. J. Mech. Eng. **2021**, *57*, 192–207.

(30) Tian, Y.; Ye, Y.; Wang, X.; Peng, S.; Wei, Z.; Zhang, X.; Liu, W. Three-dimensional N-doped, plasma-etched graphene: Highly active metal-free catalyst for hydrogen evolution reaction. *Appl. Catal. A Gen.* **2017**, *529*, 127–133.

(31) Zheng, J.; Xu, A.; Wu, A.; Li, X. Plasma-Engraved Co2N Nanostructures toward High-Performance Alkaline Hydrogen Evolution. *ACS Appl. Mater. Interfaces.* **2021**, *18*, 13.

(32) Woo, T.; Park, I.; Jung, K.; Jeon, W.; Hwang, Y.; Seol, K. Effects of plasma treatment on the peel strength of Ni on polyimide. *Electron. Mater. Lett.* **2012**, *2*, 8.

(33) Kurihara, Y.; Ohata, H.; Kawaguchi, M.; Yamazaki, S.; Kimura, L. Improvement of adhesion and long-term adhesive reliability of liquid crystalline polyester film by plasma treatment. *J. Appl. Polym. Sci.* **2008**, *108*, 85–92.

(34) Song, I. K.; Cho, Y. S.; Choi, G. S.; Kim, D. J. The growth mode change in carbon nanotube synthesis in plasma-enhanced chemical vapor deposition. *Diam. Relat. Mater.* **2004**, *13*, 1210–1213.

(35) Li, L.; Cheng Tang, C.; Cui, X.; Zheng, Y.; Wang, X.; Xu, H.; Zhang, S.; Shao, T.; Davey, K.; Qiao, S. Efficient Nitrogen Fixation to Ammonia through Integration of Plasma Oxidationwith Electrocatalytic Reduction. *Angew. Chem., Int. Ed.* **2021**, *60*, 14131–14137.

(36) Dumitrascu, N.; Topala, I.; Popa, G. Dielectric barrier discharge technique in improving the wettability and adhesion properties of polymer surfaces. *IEEE Trans. Plasma Sci.* **2005**, *33*, 1710–1714.

(37) Zhou, P.; He, J.; Zou, Y.; Wang, Y.; Xie, C.; Chen, R.; Zang, S.; Wang, S. Single-crystalline layered double hydroxides with rich defects and hierarchical structure by mild reduction for enhancing the oxygen evolution reaction. *Sci. China Chem.* **2019**, *62*, 1365–1370.

(38) Rosenberg, M.; Sheehan, D. P.; Petrie, J. R. Use of dusty plasmas for surface-enhanced vibrational spectroscopy studies. *J. Phys. Chem. A* **2004**, *108*, 5573–5575.

(39) Wu, A.; Yang, J.; Xu, B.; Wu, X.; Wang, Y.; Lv, X.; Ma, Y.; Xu, A.; Zheng, J.; Tan, Q.; Peng, Y.; Qi, Z.; Qi, H.; Li, J.; Wang, Y.; Harding, J.; Tu, X.; Wang, A.; Li, X. Direct ammonia synthesis from the air via gliding arc plasma integrated with single atom electrocatalysis. *Appl. Catal. B Environ.* **2021**, *8*, 120667.

(40) Xu, A.; Dong, C.; Wu, A.; Li, R.; Wang, L.; Macdonald, D. D.; Li, X. Plasma-modified C-doped Co_3O_4 nanosheets for the oxygen evolution reaction designed by Butler-Volmer and first-principle calculations. *J. Mater. Chem. A* **2019**, *7*, 4581–4895.

(41) Shui, S.; Huang, C.; Ma, P.; Li, W.; He, Q.; Wu, W.; Tan, Y.; Bao, J. Accelerating C2+ alcohols synthesis from syngas by simultaneous optimizations of CO dissociation and chain growth over CuCo alloy catalyst. *Chin. Chem. Lett.* **2021**, *32*, 2203–2206.

(42) Gao, W.; Zhao, Y.; Chen, H.; Chen, H.; Li, Y.; He, S.; Zhang, Y.; Wei, M.; Evans, D. G.; Duan, X. Core-shell $Cu@(CuCo-alloy)/Al_2O_3$ catalysts for the synthesis of higher alcohols from syngas. *Green Chem.* **2015**, *17*, 1525–1534.

(43) Noh, H.; Lee, K.; Chandra, P.; Won, M.; Shim, Y. Application of a Cu–Co alloy dendrite on glucose and hydrogen peroxide sensors. *Electrochim* **2012**, *61*, 36–43.

(44) Zhang, D.; Li, C.; Zhang, C.; Slipchenko, M. N.; Eakins, G.; Cheng, J. Depth-resolved mid-infrared photothermal imaging of living cells and organisms with submicrometer spatial resolution. *Sci. Adv.* **2016**, *2*, *9*.

(45) Li, C.; Zhang, D.; Slipchenko, M. N.; Cheng, J. Mid-Infrared Photothermal Imaging of Active Pharmaceutical Ingredients at Submicrometer Spatial Resolution. *Anal. Chem.* **2017**, *9*, 89.

(46) Su, Y.; Hu, X.; Tang, H.; Lu, K.; Li, H.; Liu, S.; Xing, B.; Ji, R. Steam disinfection releases micro(nano)plastics from silicone-rubber baby teats as examined by optical photothermal infrared microspectroscopy. *Nat. Nanotechnol.* **2022**, *17*, 76–85.

(47) Klementieva, O.; Sandt, S.; Martinsson, I.; Kansiz, M.; Gouras, G. K.; Borondics, F. Super-Resolution Infrared Imaging of Polymorphic Amyloid Aggregates Directly in Neurons. *Adv. Sci.* **2020**, *6*, 7.

(48) Wang, D.; He, N.; Xiao, L.; Dong, F.; Chen, W.; Zhou, Y.; Chen, C.; Wang, S. Coupling electrocatalytic NO oxidation over carbon cloth with hydrogen evolution reaction for nitrate synthesis. *Angew. Chem., Int. Ed.* **2021**, *60*, 24810–24816.

(49) (a) Wu, Z.; Karamad, K.; Yong, X.; Huang, Q.; Cullen, D. A.; Zhu, P.; Xia, C.; Xiao, Q.; Shakouri, M.; Chen, F.; Kim, J. Y.; Xia, Y.; Heck, K.; Hu, Y.; Wong, M. S.; Li, Q.; Gates, I.; Siahrostami, S.; Wang, H. Electrochemical ammonia synthesis via nitrate reduction on Fe single atom catalyst. *Nat. Commun.* **2021**, *12*, 2870. (b) Hu, C.; Zhang, L.; Li, L.; Zhu, W.; Deng, W.; Dong, H.; Zhao, Z.; Gong, J. Theory assisted design of N-doped tin oxides for enhanced electrochemical CO_2 activation and reduction. *Sci. China Chem.* **2019**, *62*, 1030–1036. (50) Figueiredo, M. C.; Solla-Gullón, J.; Vidal-Iglesias, F. J.; Climent, V.; Feliu, J. M. Nitrate reduction at Pt (100) single crystals and preferentially oriented nanoparticles in neutral media. *Catal. Today.* **2013**, 202, 2–11.

(51) Pérez-Gallent, E.; Figueiredo, M. C.; Katsounaros, I.; Koper, M. T. M. Electrocatalytic reduction of Nitrate on Copper single crystals in acidic and alkaline solutions. *Electrochim. Acta* **2017**, *227*, 77–84. (52) da Cunha, M. C. P. M.; De Souza, J. P. I.; Nart, F. C. Reaction Pathways for Reduction of Nitrate Ions on Platinum, Rhodium, and Platinum-Rhodium Alloy Electrodes. *Langmuir.* **2000**, *16*, 771–777.

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