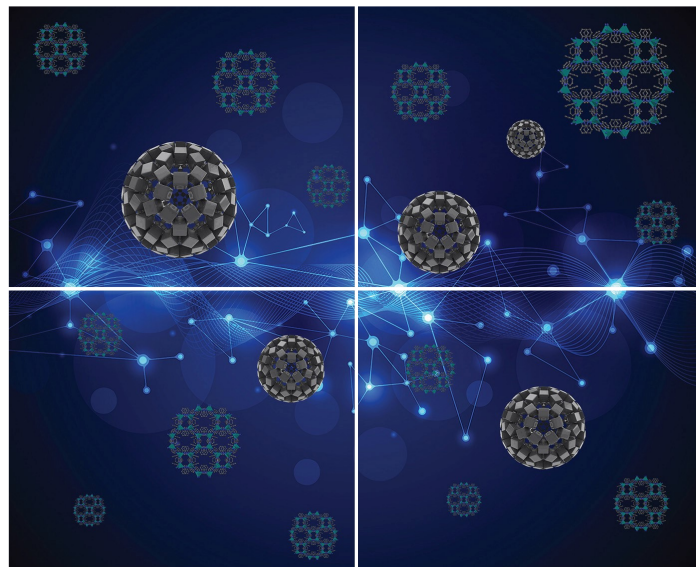


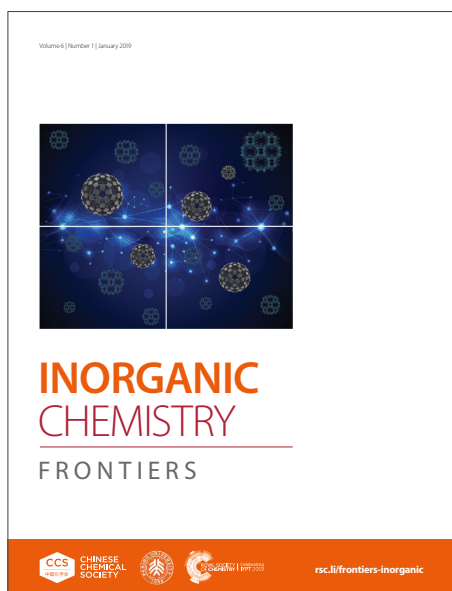
# INORGANIC CHEMISTRY

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## RESEARCH ARTICLE

Construction of Carbon Nanotube-Supported CuO-Fe<sub>3</sub>O<sub>4</sub> Dual-Site Catalysts for Ambient Electrosynthesis of AmmoniaShun Zhang,<sup>a,b</sup> Shengbo Zhang,<sup>\*a,b</sup> Jiafang Liu,<sup>a,b</sup> Zhixian Mao,<sup>a,b</sup> Yunxia Zhang,<sup>a,b</sup> Guozhong Wang,<sup>a,b</sup> Huajie Yin,<sup>a,b</sup> Haimin Zhang<sup>\*a,b</sup>Received 00th January 20xx,  
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Electrocatalytic nitrate (NO<sub>3</sub><sup>-</sup>) reduction reaction (NitRR) to ammonia (NH<sub>3</sub>) is considered a sustainable and environmentally friendly approach for synthesizing ammonia. However, the electrocatalyst encounters challenges related to the limited distribution of NO<sub>3</sub><sup>-</sup> and insufficient active hydrogen on the catalyst surface, which result from the high concentration of NO<sub>3</sub><sup>-</sup> and the difficulty of water splitting under ambient conditions. Here, by introducing Cu and Fe oxides onto carbon nanotube substrates (CuO-Fe<sub>3</sub>O<sub>4</sub>/CNT), a CuO-Fe<sub>3</sub>O<sub>4</sub> dual-site synergistic catalytic mechanism is proposed to promote the adsorption and conversion of NO<sub>3</sub><sup>-</sup> at Cu species site and accelerate water splitting at Fe species site, thereby significantly enhancing the performance of nitrate reduction reactions. The as-synthesized CuO-Fe<sub>3</sub>O<sub>4</sub>/CNT exhibits good activity for NitRR, achieving an NH<sub>3</sub> yield rate of 39.2 ± 3.5 mg h<sup>-1</sup> mg<sub>cat</sub><sup>-1</sup> and a Faradaic efficiency of 90.5 ± 2.2% at -0.8 V (vs. RHE). Furthermore, different *in-situ* characterizations were employed to identify intermediates in the electrocatalytic NitRR process, confirming CuO-Fe<sub>3</sub>O<sub>4</sub>/CNT as a promising catalyst for NH<sub>3</sub> electrosynthesis.

Ammonia (NH<sub>3</sub>) is a crucial chemical in modern society, widely used across various industries<sup>[1-3]</sup>. The conventional method for NH<sub>3</sub> synthesis is the Haber-Bosch process, which uses hydrogen obtained from water electrolysis and nitrogen from the air as feedstocks<sup>[4-5]</sup>. Although these raw materials are relatively inexpensive, the process is highly energy-intensive and produces significant CO<sub>2</sub> emissions, posing serious environmental concerns<sup>[6-7]</sup>. Additionally, the low solubility of N<sub>2</sub> in water and the high dissociation energy of the N≡N bond (941 kJ mol<sup>-1</sup>) further limits its practical application<sup>[8-9]</sup>. In contrast, nitrate (NO<sub>3</sub><sup>-</sup>), with a much lower N=O bond dissociation energy (204 kJ mol<sup>-1</sup>), is considered a promising alternative nitrogen source due to its abundance<sup>[10-11]</sup>. With

industrial development, increasing amounts of nitrate-containing wastewater are being released into the environment<sup>[12]</sup>. Utilizing nitrate as a nitrogen source offers a dual benefit: reducing energy consumption in NH<sub>3</sub> production and mitigating water pollution caused by nitrate<sup>[13-16]</sup>. Electrocatalytic nitrate reduction reaction (NitRR) for ammonia synthesis has emerged as a promising new approach in recent years, enabling both wastewater treatment and continuous ammonia generation<sup>[17-18]</sup>. However, the NitRR involves a complex eight-electron transfer process with multiple reaction pathways and intermediates, which hinders the efficient conversion of NO<sub>3</sub><sup>-</sup> to NH<sub>3</sub><sup>[19]</sup>. Therefore, there is an urgent need for a catalyst that can achieve both high Faradaic efficiency and high selectivity for ammonia production.

The electrochemical NitRR to NH<sub>3</sub> is a multi-step cascade process that commences with water activation for the generation of active hydrogen atoms (\*H), followed by the sequential hydrogenation of adsorbed NO<sub>3</sub><sup>-</sup> species<sup>[20]</sup>. The competition for active sites on traditional single-active-site electrocatalysts significantly reduces the efficiency and selectivity of NH<sub>3</sub> electrosynthesis from NO<sub>3</sub><sup>-</sup><sup>[21]</sup>. In particular, in nitrate waste water systems, the conversion of NO<sub>3</sub><sup>-</sup> to NH<sub>3</sub> is constrained by sluggish water dissociation kinetics and weak NO<sub>3</sub><sup>-</sup> adsorption. Recently, dual-active-site catalysts have attracted increasing attention for electrochemical NitRR<sup>[22-23]</sup>. Previous studies demonstrate that transition metals with high electrical conductivity and platinum-like electronic structures can efficiently generate adsorbed hydrogen through water dissociation, thereby promoting nitrate reduction<sup>[24-25]</sup>. Furthermore, theoretical calculations indicate that iron (Fe) atoms exhibit low energy barriers for nitrogen-oxygen intermediates (e.g., \*NO<sub>2</sub>, \*NO), resulting in high selectivity toward NH<sub>3</sub><sup>[26-27]</sup>. However, Fe-based catalysts show limited affinity for nitrate adsorption, which hinders the initial reduction of NO<sub>3</sub><sup>-</sup> to NO<sub>2</sub><sup>-</sup> and promotes the competing hydrogen evolution reaction (HER)<sup>[26-27]</sup>. Copper (Cu) atoms, whose *d*-orbitals exhibit favorable energy alignment with the π\* orbitals of nitrate, enhance both the adsorption and reduction of NO<sub>3</sub><sup>-</sup> to NO<sub>2</sub><sup>-</sup><sup>[25, 28]</sup>. Therefore, incorporating Cu atoms into Fe-based catalysts can provide sufficient NO<sub>2</sub><sup>-</sup> intermediates for subsequent deoxygenation and hydrogenation steps. Based on

<sup>a</sup> Key Laboratory of Materials Physics, Centre for Environmental and Energy Nanomaterials, Anhui Key Laboratory of Nanomaterials and Nanotechnology, CAS Center for Excellence in Nanoscience Institute of Solid State Physics, HFIPS, Chinese Academy of Sciences, Hefei 230031, China. E-mail: shbzhzhang@issp.ac.cn, zhanghm@issp.ac.cn

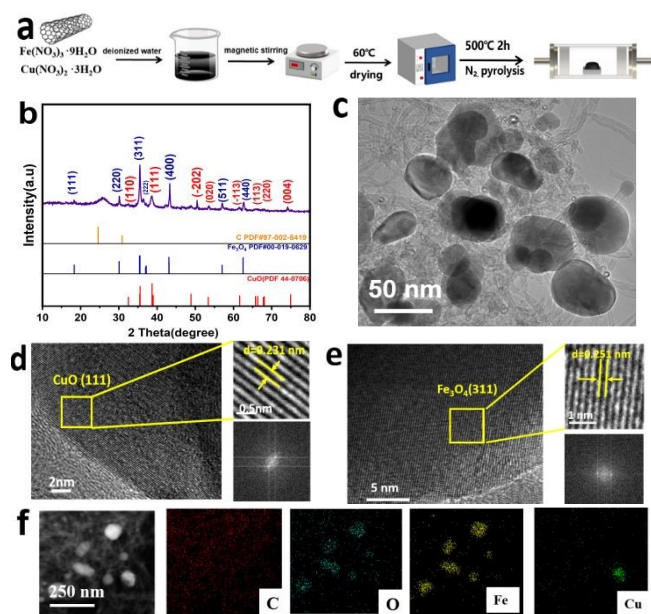
<sup>b</sup> University of Science and Technology of China, Hefei 230026, China  
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## Research Article

the basic electrochemical property analysis of Cu and Fe, we anticipate that the Cu-Fe-based dual-site catalyst will significantly improve NitRR performance at ambient conditions.

In this study, we propose a Cu-Fe dual-site synergistic catalytic mechanism, in which CuO is introduced into Fe<sub>3</sub>O<sub>4</sub> to enhance NO<sub>3</sub><sup>-</sup> adsorption and conversion at Cu site, while optimizing \*H adsorption on Fe site, thereby achieving significantly improved NitRR performance. Intriguingly, during the initial stage of electrolysis, the pre-loaded CuO nanoparticles were partially reduced, forming rod-like metallic copper (Cu). Concurrently, the outer layer of the Fe<sub>3</sub>O<sub>4</sub> phase underwent oxidation to Fe<sub>2</sub>O<sub>3</sub>. The resulting Cu and CuO species work together as the copper active sites, while the Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub> phases collectively function as the iron-based active sites. The CuO-Fe<sub>3</sub>O<sub>4</sub> dual-site demonstrated outstanding performance, achieving an NH<sub>3</sub> yield rate of 39.2 ± 3.5 mg h<sup>-1</sup> mg<sub>cat</sub><sup>-1</sup> and a Faradaic efficiency of 90.5 ± 2.2% at -0.8 V (vs. RHE). <sup>15</sup>N isotopic labelling experiments were conducted to verify the nitrogen source of the synthesized NH<sub>3</sub>, with quantification performed using the colorimetric method. *In-situ* attenuated total reflectance surface-enhanced infrared absorption spectroscopy (ATR-SEIRAS) revealed that the CuO-Fe<sub>3</sub>O<sub>4</sub> dual-site exhibit exclusive selectivity for NH<sub>3</sub> during the electrocatalytic NitRR, which is further unveiled by in situ differential electrochemical mass spectrometry (DEMS) analysis.



**Fig. 1** (a) Schematic illustration of the synthetic process of the CuO-Fe<sub>3</sub>O<sub>4</sub>/CNTs sample. (b) XRD pattern of CuO-Fe<sub>3</sub>O<sub>4</sub>/CNTs. (c) TEM image of CuO-Fe<sub>3</sub>O<sub>4</sub>/CNTs. (d) TEM and (e) HR-TEM images of CuO-Fe<sub>3</sub>O<sub>4</sub>/CNTs. (f) EDX images of CuO-Fe<sub>3</sub>O<sub>4</sub>/CNTs.

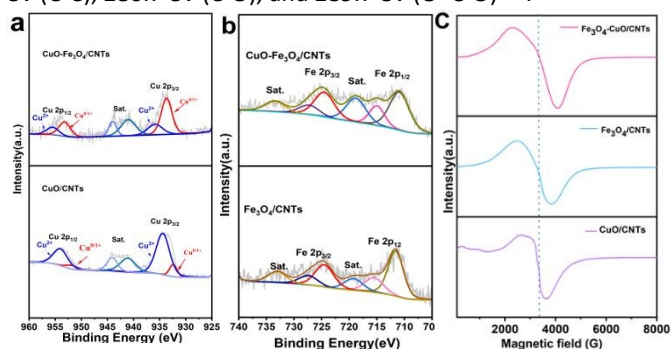
Fig. 1a depicts a schematic representation of the synthesis process employed for synthesizing the CuO-Fe<sub>3</sub>O<sub>4</sub> dual-site supported on carbon nanotubes (CuO-Fe<sub>3</sub>O<sub>4</sub>/CNTs) *via* a simple two-step method of impregnation adsorption and high-temperature calcination. The actual loading amounts of Cu and Fe in the CuO-Fe<sub>3</sub>O<sub>4</sub>/CNTs catalyst are 26.0% and 11.4% by

inductively coupled plasma atomic emission spectroscopy (ICP-AES), respectively. For comparison, CuO and Fe<sub>3</sub>O<sub>4</sub> single-site anchored on the CNTs (CuO/CNTs and Fe<sub>3</sub>O<sub>4</sub>/CNTs) with the Cu and Fe loading of 32.3% and 30.6% were also synthesized through similar synthetic process as CuO-Fe<sub>3</sub>O<sub>4</sub>/CNTs (Fig. S1, ESI<sup>†</sup>). Fig. 1b presents the X-ray diffraction (XRD) pattern of the CuO-Fe<sub>3</sub>O<sub>4</sub>/CNTs sample. The strong peak at 26.1° matches the characteristic signal of carbon (JCPDS Card 97-002-8419), which is attributed to the highly graphitized carbon nanotubes (CNTs) substrate<sup>[29]</sup>. Additional peaks at approximately 32.7°, 38.6°, 49.9°, 53.4°, 58.2°, 61.6°, and 74.1° correspond to the (1 1 0), (1 1 1), (-2 0 2), (0 2 0), (-1 1 3), and (0 0 4) planes of CuO (JCPDS No. 44-0706)<sup>[30]</sup>. Meanwhile, the characteristic peaks at 30.01°, 35.26°, 36.73°, 43.24°, 57.01°, and 62.75° match the (2 2 0), (3 1 1), (2 2 2), (4 0 0), (5 1 1), and (4 4 0) planes of cubic Fe<sub>3</sub>O<sub>4</sub> (JCPDS No. 00-019-0629)<sup>[31]</sup>, respectively, which confirms the existence of Fe species in the form of oxides in the Fe<sub>3</sub>O<sub>4</sub>/CNTs catalyst. The microscopic morphology of CuO-Fe<sub>3</sub>O<sub>4</sub>/CNTs was characterized via scanning electron microscopy (SEM) (Fig. S2, ESI<sup>†</sup>). In the SEM images, the CNTs substrate could be clearly discerned (Fig. S3, ESI<sup>†</sup>). The CNTs presented an evident cylindrical tubular structure, with CuO and Fe<sub>3</sub>O<sub>4</sub> nanoparticles deposited on their surfaces. As depicted in Fig. S3 (ESI<sup>†</sup>), at the microstructural scale, the CNTs were stacked and randomly dispersed. This arrangement not only enhanced the conductivity of the catalyst but also provided an abundance of active sites<sup>[32]</sup>. The hollow tubular structure and open pores of the CNTs facilitated the diffusion of reactants and products, thus improving the mass transfer efficiency in liquid-phase reactions. Moreover, the transmission electron microscopy (TEM) image of CuO-Fe<sub>3</sub>O<sub>4</sub>/CNTs (Fig. 2c) further demonstrated that CuO and Fe<sub>3</sub>O<sub>4</sub> were firmly anchored on the CNTs. The high-resolution transmission electron microscopy (HR-TEM) images (Fig. 2d and Fig. 2e) exhibit lattice fringes measuring 0.251 nm and 0.231 nm. These lattice fringes correspond to the (3 1 1) plane of Fe<sub>3</sub>O<sub>4</sub> and the (1 1 1) plane of CuO, respectively, which is in good agreement with the XRD results. Additionally, high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and the corresponding energy-dispersive X-ray (EDX) mapping images (Fig. 2f) reveal that the elements of Cu, Fe, C, and O are homogeneously distributed on the carbon nanotubes. The N<sub>2</sub> adsorption-desorption isotherm measurement results (Fig. S4, ESI<sup>†</sup>) reveal that the BET surface area of CuO-Fe<sub>3</sub>O<sub>4</sub>/CNTs is 178.8 m<sup>2</sup>/g. The sample displays a typical type IV isotherm with distinct hysteresis loops, which indicates the existence of mesoporous structures, and the pore volume is 0.82 cm<sup>3</sup>/g. The high surface area and porous architecture of this catalyst are conducive to charge and mass transport during electrocatalytic processes<sup>[32]</sup>.

To further investigate the surface elemental composition and valence states, X-ray photoelectron spectroscopy (XPS) was carried out on CuO-Fe<sub>3</sub>O<sub>4</sub>/CNTs, CuO/CNTs, and Fe<sub>3</sub>O<sub>4</sub>/CNTs samples. Fig. S5a (ESI<sup>†</sup>) presents the survey spectra of CuO-Fe<sub>3</sub>O<sub>4</sub>/CNTs, confirming the presence of C, O, Fe, and Cu elements. The O 1s spectrum (Fig. S5c, ESI<sup>†</sup>) shows a peak at 531.7 eV attributed to oxygen vacancies (V<sub>O</sub>), and another at 530.3 eV corresponding to Fe-O bonds<sup>[33-34]</sup>. The superior nitrate reduction activity observed for the CuO-Fe<sub>3</sub>O<sub>4</sub>/CNTs catalyst can be attributed in part to its high concentration of oxygen vacancies, as confirmed by electron paramagnetic



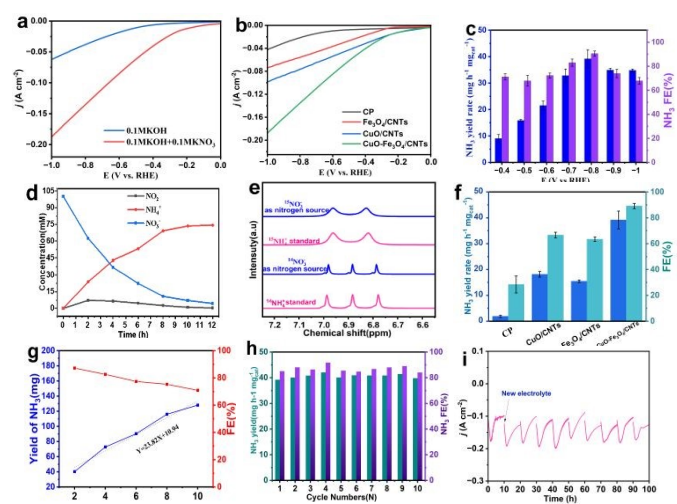
resonance (EPR) spectroscopy (Fig. 2c). All samples exhibited a characteristic EPR signal at a  $g$ -value of 2.002, which is associated with unpaired electrons located at oxygen vacancy sites [35]. Notably, the CuO-Fe<sub>3</sub>O<sub>4</sub>/CNTs composite showed the highest signal intensity, indicating a greater abundance of oxygen vacancies compared to the other catalysts. The slanted baseline of the EPR spectra, a common feature in magnetic materials, was appropriately corrected during data analysis. These oxygen vacancies play an essential role in enhancing catalytic performance by modulating the surface electronic structure, which facilitates electron transfer to adsorbed nitrate ions and strengthens their interaction with the catalyst surface, thereby significantly promoting the reduction activity [36–37]. In the Cu 2p spectrum (Fig. 2a), the peaks for CuO/CNTs are mainly associated with Cu<sup>2+</sup>, while those for Cu<sup>0,1+</sup> are relatively weak. Upon integration with Fe<sub>3</sub>O<sub>4</sub>, a notable electronic modulation of Cu species is observed, as reflected in the shifts in Cu 2p peaks. Specifically, the Cu<sup>0/1+</sup> states (2p<sub>3/2</sub>: 933.7 eV, 2p<sub>1/2</sub>: 953.3 eV) show significantly enhanced intensity, whereas the Cu<sup>2+</sup> signals (2p<sub>3/2</sub>: 936.0 eV, 2p<sub>1/2</sub>: 955.7 eV) are attenuated [30,38]. This decrease in the Cu<sup>2+</sup>/Cu<sup>0</sup> ratio indicates electron transfer from Fe<sub>3</sub>O<sub>4</sub> to CuO centers, which is further confirmed by the results of differential charge analysis (Fig. S6, ESI<sup>†</sup>). The Fe 2p spectrum (Fig. 2b) reveals two pairs of peaks at ~710.6 eV and ~723.6 eV, as well as ~714.7 eV and ~726.4 eV, which correspond to the Fe 2p<sub>3/2</sub> and Fe 2p<sub>1/2</sub> peaks of Fe<sup>2+</sup> and Fe<sup>3+</sup>, respectively [33]. The high-resolution C 1s spectrum (Fig. S5b, ESI<sup>†</sup>) can be deconvoluted into three components at 284.8 eV (C-C), 286.7 eV (C-O), and 289.7 eV (O=C-O) [39].



**Fig. 2** (a) The Cu 2p XPS spectra of the different catalysts. (b) Fe 2p spectra of the different samples. (c) EPR spectroscopy of different catalysts.

The NitRR performance of all as-prepared catalysts was evaluated using an electrochemical workstation in an H-type electrolytic cell under ambient temperature and pressure. First, the NitRR electrochemical performance was assessed by linear sweep voltammetry (LSV). Prior to each test, cyclic voltammetry (CV) scans were conducted until the polarization curves stabilized. The concentrations of NH<sub>3</sub> and the by-product NO<sub>2</sub><sup>-</sup> were determined via colorimetric analysis. Corresponding calibration curves are presented in Figs. S7, S8, and S9 (ESI<sup>†</sup>). As shown in Fig. 3a, the LSV curve of CuO-Fe<sub>3</sub>O<sub>4</sub>/CNTs in 0.1 M KOH with nitrate exhibits a significantly higher current density compared to that without nitrate, indicating nitrate

participation in the electrochemical reaction. Similarly, LSV curves of CuO/CNTs and Fe<sub>3</sub>O<sub>4</sub>/CNTs (Fig. 3b) show the same trend, however, their current densities are notably lower than that of CuO-Fe<sub>3</sub>O<sub>4</sub>/CNTs, suggesting a synergistic effect between CuO and Fe<sub>3</sub>O<sub>4</sub> in promoting nitrate reduction. With respect to onset potential, CuO/CNTs and CuO-Fe<sub>3</sub>O<sub>4</sub>/CNTs exhibit similar values, indicating that CuO plays a key role in nitrate adsorption and activation.



**Fig. 3** (a) LSV curves of CuO-Fe<sub>3</sub>O<sub>4</sub>/CNTs in Ar-saturated 0.1 M KOH with and without nitrate. (b) LSV curves of the CP, CuO-Fe<sub>3</sub>O<sub>4</sub>/CNTs, Fe<sub>3</sub>O<sub>4</sub>/CNTs and CuO/CNTs for nitrate reduction in 0.1 M KOH electrolyte containing 0.1 M KNO<sub>3</sub>. (c) NH<sub>3</sub> yield rate and FE of the CuO-Fe<sub>3</sub>O<sub>4</sub>/CNTs catalyst obtained at different applied potentials (d) Concentration changes of NO<sub>3</sub><sup>-</sup>, NO<sub>2</sub><sup>-</sup>, NH<sub>3</sub> of CuO-Fe<sub>3</sub>O<sub>4</sub>/CNTs at -0.8 V (vs. RHE). (e) <sup>1</sup>H NMR spectra of <sup>14</sup>NH<sub>4</sub><sup>+</sup> and <sup>15</sup>NH<sub>4</sub><sup>+</sup> standards, and the resultant samples from CuO-Fe<sub>3</sub>O<sub>4</sub>/CNTs-catalyzed NitRR using <sup>14</sup>NO<sub>3</sub><sup>-</sup> and <sup>15</sup>NO<sub>3</sub><sup>-</sup> as nitrogen source, respectively. (f) Ammonia yield rate and Faradaic efficiencies of CP, CuO/CNTs, Fe<sub>3</sub>O<sub>4</sub>/CNTs, and CuO-Fe<sub>3</sub>O<sub>4</sub>/CNTs at -0.8 V (vs. RHE). (g) The NH<sub>3</sub> yield and FE for NH<sub>3</sub> production over CuO-Fe<sub>3</sub>O<sub>4</sub>/CNTs toward electrocatalytic NitRR with reaction time at -0.8 V (vs. RHE). (h) Cycling stability test of CuO-Fe<sub>3</sub>O<sub>4</sub>/CNTs at -0.8 V (vs. RHE) for 10 cycles. (i) The i-t curve of long-time stability test for 100 h at -0.8 V (vs. RHE).

To further demonstrate its superior electrochemical performance, chronoamperometry (i-t) was conducted at applied potentials ranging from -0.4 to -1.0 V (vs. RHE) to determine the ammonia yield rate and Faraday efficiency (Fig. S10, ESI<sup>†</sup>). The corresponding NH<sub>3</sub> yield rate ( $R_{\text{NH}_3}$ ) and Faraday efficiency (FE) under these potentials are shown in Fig. 3c. Both  $R_{\text{NH}_3}$  and FE exhibit a volcano-shaped dependence on potential, peaking at -0.8 V (vs. RHE), likely due to competition with the hydrogen evolution reaction. Notably, CuO-Fe<sub>3</sub>O<sub>4</sub>/CNTs achieves an impressive  $R_{\text{NH}_3}$  of  $39.2 \pm 3.5$  mg h<sup>-1</sup> mg<sub>cat</sub><sup>-1</sup> and a high FE of  $90.5 \pm 2.2\%$  at -0.8 V (vs. RHE) in 0.1 M KOH + 0.1 M KNO<sub>3</sub>, outperforming most previously reported NitRR electrocatalysts (Table S1, ESI<sup>†</sup>). Importantly, NH<sub>3</sub> is the dominant product, with minimal NO<sub>2</sub><sup>-</sup> detected in the final solution (Fig. S11, ESI<sup>†</sup>), indicating excellent selectivity for the NitRR. Fig. 3d presents the concentration-time profiles of NH<sub>3</sub>, NO<sub>3</sub><sup>-</sup>, and NO<sub>2</sub><sup>-</sup>. The continuous decrease in NO<sub>3</sub><sup>-</sup> and increase in NH<sub>3</sub> confirm that nitrate



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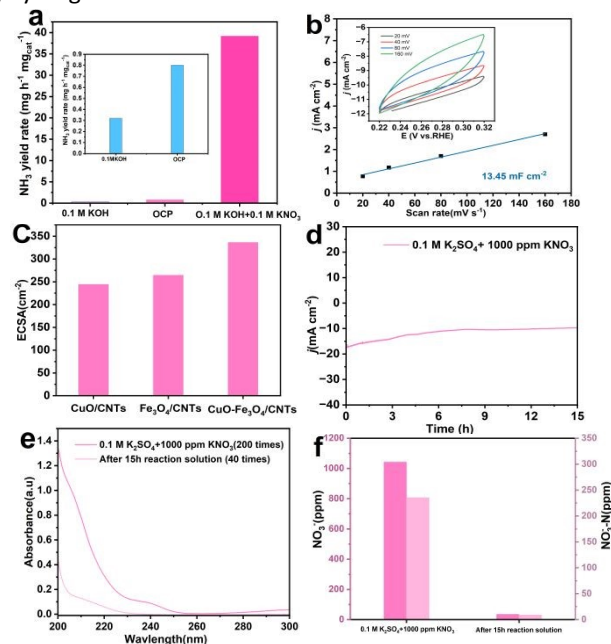
is steadily converted into ammonia. Meanwhile, the initial rise followed by a decline in  $\text{NO}_2^-$  suggests that it is an intermediate species subsequently reduced to  $\text{NH}_3$ . The  $^1\text{H}$  NMR spectra of standards and the produced  $^{14}\text{NH}_4^+$  and  $^{15}\text{NH}_4^+$  in NitRR samples (Fig. 3e) confirm that the generated  $\text{NH}_3$  originates from the 0.1 M  $\text{KNO}_3$  feedstock. Additionally, the amount of  $^{15}\text{NH}_3$  was quantified using the indophenol blue method, yielding results consistent with those for  $^{14}\text{NH}_3$  at  $-0.8$  V (vs. RHE) (Fig. S12, ESI<sup>†</sup>).

Furthermore, the NitRR activity of the four catalysts was evaluated at  $-0.8$  V (vs. RHE), as shown in Fig. 3f. The  $\text{NH}_3$  Faradaic efficiencies of  $\text{CuO-Fe}_3\text{O}_4/\text{CNTs}$ ,  $\text{CuO}/\text{CNTs}$ ,  $\text{Fe}_3\text{O}_4/\text{CNTs}$ , and CP were 90.5%, 66.7%, 63.5%, and 28.4%, respectively. It is also worth noting that the ammonia yield of  $\text{CuO-Fe}_3\text{O}_4/\text{CNTs}$  is  $39.2 \text{ mg h}^{-1} \text{ mg}_{\text{cat.}}^{-1}$ , which is 2.2 times that of  $\text{CuO}/\text{CNTs}$  ( $18.2 \text{ mg h}^{-1} \text{ mg}_{\text{cat.}}^{-1}$ ), 2.65 times that of  $\text{Fe}_3\text{O}_4/\text{CNTs}$  ( $15.5 \text{ mg h}^{-1} \text{ mg}_{\text{cat.}}^{-1}$ ), and 20.6 times that of CNTs ( $1.9 \text{ mg h}^{-1} \text{ mg}_{\text{cat.}}^{-1}$ ). It is certified the superior NitRR performance of  $\text{CuO-Fe}_3\text{O}_4/\text{CNTs}$  coming from the synergistic effect of  $\text{CuO}$  and  $\text{Fe}_3\text{O}_4$  in catalyst. Additionally, the durability of  $\text{CuO-Fe}_3\text{O}_4/\text{CNTs}$  for 12 hours at  $-0.8$  V (vs. RHE) was confirmed by the chronoamperometry measurements (Fig. S13, ESI<sup>†</sup>). The obtained  $\text{NH}_3$  yield and reaction time show a linear relationship, with a slight decrease in FE (Fig. 3g), demonstrating the excellent stability of  $\text{CuO-Fe}_3\text{O}_4/\text{CNTs}$ . At the same time,  $\text{CuO-Fe}_3\text{O}_4/\text{CNTs}$  also demonstrated good catalytic stability, with only minor variations in FE observed over ten cycles (Fig. 3h).

The long-time stability of a catalyst is a critical indicator for assessing its practical applicability. As demonstrated in Fig. 3i, a 100-hour durability test was conducted on the  $\text{CuO-Fe}_3\text{O}_4/\text{CNTs}$  catalyst, with the electrolyte replenished every 10 hours. After each refresh, the current density that had increased during reaction, returned to its original level, indicating good stability. SEM characterization further confirmed the structural robustness of the material. Comparisons among the post-reaction samples after 100 hours Fig. S14a, ESI<sup>†</sup>), 10 cycles (20 hours, Fig. S14b, ESI<sup>†</sup>), and the fresh catalyst (Fig. S2, ESI<sup>†</sup>) revealed no significant morphological changes in the carbon nanotubes. The CNTs network remained intact without apparent change, underscoring the essential role of the CNTs framework in providing mechanical support and electrical conductivity throughout the prolonged test. Notably, phase transformations occurred within the  $\text{CuO}$  and  $\text{Fe}_3\text{O}_4$ , some of the initially loaded  $\text{CuO}$  nanoparticles were reduced to metallic  $\text{Cu}$ , forming nanorod-like structures, as indicated by the lattice fringes of the (111) plane of  $\text{Cu}$  in figure (Fig. S14c, ESI<sup>†</sup>). Simultaneously, the surface of the  $\text{Fe}_3\text{O}_4$  particles was oxidized to  $\text{Fe}_2\text{O}_3$ , which was identified by the lattice spacing corresponding to the (104) plane of  $\text{Fe}_2\text{O}_3$  (Fig. S14e, ESI<sup>†</sup>).

Crucially, the chemical state analysis via XPS, which we conducted on the catalyst after continuous 10 cycles of operation, already provides definitive evidence of reconstruction. As illustrated in Fig. S15a (ESI<sup>†</sup>), the  $\text{Cu}$  2p spectrum exhibits a negative binding energy shift along with an increased ratio of  $\text{Cu}^0/\text{Cu}^+$  to  $\text{Cu}^{2+}$ , indicating electron transfer from  $\text{Fe}_3\text{O}_4$  to  $\text{CuO}$  during the reaction. Correspondingly, the  $\text{Fe}$  2p spectrum (Fig. S15b, ESI<sup>†</sup>) shows a decreased  $\text{Fe}^{2+}/\text{Fe}^{3+}$  ratio and the disappearance of satellite features, confirming the

oxidation of  $\text{Fe}_3\text{O}_4$  to  $\text{Fe}_2\text{O}_3$  within 20 hours. These findings not only verify the 1 electron transfer between  $\text{CuO}$  and  $\text{Fe}_3\text{O}_4$ , but also demonstrate that in situ reconstruction occurs rapidly within the initial hours of operation. Also, the coexistence of  $\text{CuO}$  and  $\text{Fe}_3\text{O}_4$  accelerates electron transfer from the  $\text{Fe}$  component to the  $\text{Cu}$  component, which enhances the adsorption/activation of nitrate on the negative  $\text{Cu}$  sites and the affinity of atomic hydrogen on the positive  $\text{Fe}$  sites. It thus significantly improves intrinsic catalytic activity of the catalyst by synergistic effect.



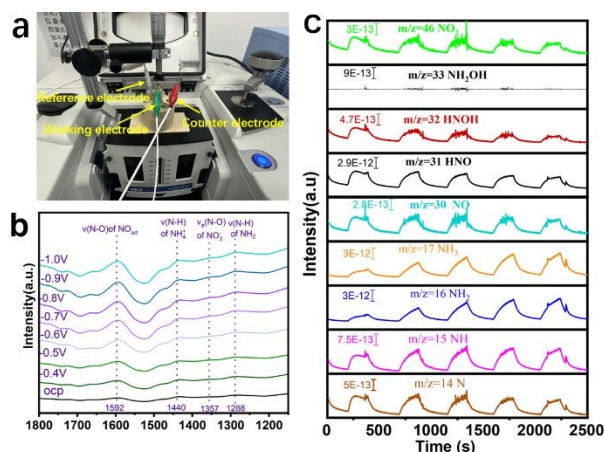
**Fig. 4** (a) Comparison of ammonia contents of  $\text{CuO-Fe}_3\text{O}_4/\text{CNTs}$  and the black control groups under alkaline conditions (inset is an enlarged image of the control groups). (b) Plots of current density versus scan rate for  $\text{CuO-Fe}_3\text{O}_4/\text{CNTs}$  catalysts, the inset CV curves in 0.1 M KOH + 0.1 M  $\text{KNO}_3$  electrolyte at different scan rates. (c) ECSA of different catalysts. (d) I-t curve of 15h in 0.1 M  $\text{K}_2\text{SO}_4$  + 1000 ppm  $\text{KNO}_3$ . (e) UV-Vis spectra of the nitrate solution before and after a 15-h electrolysis process in 0.1 M  $\text{K}_2\text{SO}_4$  + 1000 ppm  $\text{KNO}_3$ . (f) The corresponding  $\text{NO}_3^-$  concentration calculated based on (e).

To confirm that the produced  $\text{NH}_3$  originates from the electrocatalytic nitrate reduction reaction (NitRR) on  $\text{CuO-Fe}_3\text{O}_4/\text{CNTs}$ , two control experiments were conducted: (i) in 0.1 M KOH electrolyte, and (ii) in 0.1 M KOH + 0.1 M  $\text{KNO}_3$  electrolyte under open-circuit conditions (Fig. 4a). In both cases, only negligible amounts of  $\text{NH}_3$  were detected. To compare the intrinsic activities of the catalysts, electrochemical active surface areas (ECSAs) were evaluated. The double-layer capacitance ( $\text{Cdl}$ ) was determined from cyclic voltammetry measurements at scan rates ranging from 20 to  $160 \text{ mV s}^{-1}$  (Fig. 4b, Fig. S16, ESI<sup>†</sup>). Based on these values, the ECSA of  $\text{CuO-Fe}_3\text{O}_4/\text{CNTs}$  was calculated to be  $336.25 \text{ cm}^2$ , which is larger than those of  $\text{CuO}/\text{CNTs}$  ( $224.25 \text{ cm}^2$ ) and  $\text{Fe}_3\text{O}_4/\text{CNTs}$  ( $264.25 \text{ cm}^2$ ), indicating a greater number of accessible electrocatalytic active sites (Fig. 4c).

The ultimate goal of nitrate reduction ( $\text{NO}_3\text{RR}$ ) also encompasses the practical removal of nitrate from wastewater. As real industrial



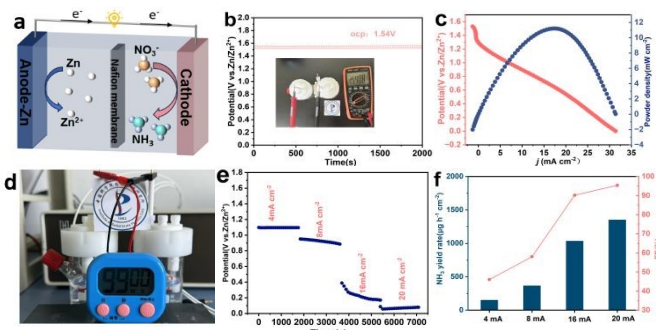
effluents often contain nitrate at low concentrations under near-neutral pH conditions, we further evaluated the catalyst using a 1000 ppm  $\text{NO}_3^-$  solution (16.1 mM) in 0.1 M  $\text{K}_2\text{SO}_4$  electrolyte to better simulate such environments. The *i-t* curve exhibited outstanding stability throughout the 15-hour test, showing only minor fluctuations and underscoring the structural robustness and operational stability of the catalyst under realistic wastewater conditions (Fig. 4d). Following electrolysis, the remaining nitrate concentration was quantified using UV-Vis spectroscopy (Fig. 4e), revealing a final concentration of 34.36 ppm (Fig. 4f), which is well below the 50 ppm  $\text{NO}_3^-$  limit established by the World Health Organization (WHO) for drinking water. This result confirms the role of the catalyst in reducing nitrate to levels compliant with international safety standards.



**Fig. 5** (a) Physical photograph of in-suit ATR-SEIRAS reactor for (b) In-situ ATR-SEIRAS spectra of electrocatalytic NitRR on  $\text{CuO-Fe}_3\text{O}_4/\text{CNTs}$  at different potentials in the 0.1 M  $\text{KOH} + 0.1 \text{ M KNO}_3$  electrolyte. (c) In-situ DEMS measurements for  $\text{CuO-Fe}_3\text{O}_4/\text{CNTs}$  in the 0.1 M  $\text{KOH} + 0.1 \text{ M KNO}_3$  electrolyte at  $-0.8 \text{ V}$  (vs. RHE) for the NitRR.

The *in-situ* attenuated total reflectance surface-enhanced infrared absorption spectroscopy (ATR-SEIRAS) was employed to investigate the reaction intermediates during the nitrate reduction reaction (NitRR). The experimental setup and cell configuration are shown in Fig. 5a. Fig. 5b displays the infrared spectra obtained during the negative potential scan from  $-0.4$  to  $-1.0 \text{ V}$  (vs. RHE) on  $\text{CuO-Fe}_3\text{O}_4/\text{CNTs}$ . A band at  $1592 \text{ cm}^{-1}$  is attributed to the N–O vibration of adsorbed NO in a bridge configuration at the open circuit potential (OCP)<sup>[40–41]</sup>. As the potential increases, a weak absorption band at  $1357 \text{ cm}^{-1}$  appears, corresponding to the asymmetric N–O stretching vibration of  $\text{NO}_3^-$ <sup>[19,41]</sup>, indicating  $\text{NO}_3^-$  consumption during the reaction. Meanwhile, a signal at  $1288 \text{ cm}^{-1}$  is assigned to the wagging mode of  $-\text{NH}_2$ , a key intermediate in ammonia formation<sup>[42]</sup>. Importantly, a gradually enhanced band at  $1440 \text{ cm}^{-1}$  corresponds to the N–H bending vibration of  $\text{NH}_3$ , providing direct evidence for ammonia production<sup>[43–45]</sup>. In addition, *in-situ* differential electrochemical mass spectrometry (DEMS) was conducted to detect gaseous intermediates and products. Fig. 5c shows the *m/z* signals at 14, 15, 16, 17, 30, 31, 32, 33, and 46, which are assigned to N, NH,  $\text{NH}_2$ ,  $\text{NH}_3$ , NO, HNO, HNOH,  $\text{NH}_2\text{OH}$ , and  $\text{NO}_2$ , respectively. Compared to other intermediates, the strongest  $\text{NH}_3$  signal confirms the high selectivity of  $\text{CuO-Fe}_3\text{O}_4/\text{CNTs}$  for ammonia production. Notably, no

$\text{NH}_2\text{OH}$  intermediate was detected. Based on the *in situ* ATR-SEIRAS and DEMS results, the following NitRR pathway on  $\text{CuO-Fe}_3\text{O}_4/\text{CNTs}$  is proposed:  $\text{NO}_3^- \rightarrow \text{NO}_3^* \rightarrow \text{NO}_2^* \rightarrow \text{NO}^* \rightarrow \text{HNO}^* \rightarrow \text{HNOH}^* \rightarrow \text{N}^* \rightarrow \text{NH}^* \rightarrow \text{NH}_2^* \rightarrow \text{NH}_3^* \rightarrow \text{NH}_3$ . These *in situ* spectroscopic findings provide strong evidence for the successful synthesis of  $\text{NH}_3$  via NitRR, supporting the previously reported electrocatalytic performance.



**Fig. 6** (a) Schematic illustration of the  $\text{Zn-NO}_3^-$  battery assembled with the  $\text{CuO-Fe}_3\text{O}_4/\text{CNTs}$  cathode. (b) OCV curve of the  $\text{Zn-NO}_3^-$  battery assembled with the  $\text{CuO-Fe}_3\text{O}_4/\text{CNTs}$  cathode. Inset of (b) shows the photograph of the OCV measurement of the  $\text{Zn-NO}_3^-$  battery. (c) Discharging curves and the corresponding power density plot. (d) Digital photos of the electronic timer powered by this  $\text{Zn-NO}_3^-$  battery. (e) Discharging tests at different current densities of this  $\text{Zn-NO}_3^-$  battery. (f)  $\text{NH}_3$  FE and  $\text{NH}_3$  yield rates in the discharge process (we assembled a rechargeable  $\text{Zn-NO}_3^-$  battery using highly active  $\text{CuO-Fe}_3\text{O}_4/\text{CNTs}$  as the cathode).

Leveraging the eight-electron transfer process for nitrate-to-ammonia conversion and the high energy density of ammonia, we constructed a rechargeable  $\text{Zn-NO}_3^-$  battery system. As illustrated in Fig. 6a, the battery employs a Zn foil anode and a  $\text{CuO-Fe}_3\text{O}_4/\text{CNTs}$  cathode for electrocatalytic nitrate reduction ( $\text{NO}_3\text{RR}$ ). This system not only delivers electrical power but also enables simultaneous ammonia synthesis and wastewater purification. The open-circuit voltage (OCV) of the  $\text{Zn-NO}_3^-$  battery with the  $\text{CuO-Fe}_3\text{O}_4/\text{CNTs}$  cathode reached approximately  $1.54 \text{ V}$  vs. Zn (Fig. 6b). Notably, the battery achieved a maximum power density of  $11.21 \text{ mW cm}^{-2}$  (Fig. 6c), surpassing values reported in previous studies<sup>[46,47]</sup>. To evaluate its practical power supply capability, the battery was used to drive a commercial electronic timer (typically powered by a  $1.5 \text{ V}$  dry battery), sustaining operation continuously for 99 minutes (Fig. 6d). During discharge, the anodic dissolution of Zn drives the nitrate reduction reaction (NitRR) at the  $\text{CuO-Fe}_3\text{O}_4/\text{CNTs}$  cathode. The battery exhibited a stable discharge profile, with gradually decreasing potential and steadily increasing current output. This result remained consistent across multiple current densities, standing out its superior discharge performance (Fig. 6e). To further confirm the dual functionality of the  $\text{Zn-NO}_3^-$  battery, including co-producing ammonia and electricity, the Faradaic efficiency of ammonia ( $\text{FE}_{\text{NH}_3}$ ) and the  $\text{NH}_3$  yield rate were measured under increasing current densities (Fig. 6f). At current densities up to  $20 \text{ mA cm}^{-2}$ , the system achieved a high  $\text{FE}_{\text{NH}_3}$  of 95.4% and an  $\text{NH}_3$  production rate of  $1351.4 \mu\text{g h}^{-1} \text{ cm}^{-2}$ . These results underscore



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the promising potential of CuO-Fe<sub>3</sub>O<sub>4</sub>/CNTs as an efficient cathode material for Zn-NO<sub>3</sub><sup>-</sup> batteries in the fields of energy storage and conversion.

In conclusion, the CuO-Fe<sub>3</sub>O<sub>4</sub> dual-site catalyst is experimentally proven as a superb NitRR electrocatalyst for ambient NH<sub>3</sub> production with a large yield of 39.2 ± 3.5 mg h<sup>-1</sup> mg<sub>cat</sub><sup>-1</sup> and a Faradaic efficiency of 90.5 ± 2.2% at -0.8 V (vs. RHE). Distinct from conventional static catalysts, the CuO-Fe<sub>3</sub>O<sub>4</sub>/CNTs material experiences dynamic reconstruction under reaction conditions, giving rise to a hybrid structure consisting of Cu/CuO and Fe<sub>2</sub>O<sub>3</sub>/Fe<sub>3</sub>O<sub>4</sub>. This self-optimizing property offers a promising framework for the design of catalysts featuring higher activity and longer-term stability. The in-situ ATR-SEIRAS and DEMS analysis is employed to identify the intermediate produced during the electrocatalytic NitRR process, confirmed CuO-Fe<sub>3</sub>O<sub>4</sub>/CNTs as a promising electrocatalyst for NH<sub>3</sub> synthesis. The results indicate that the Cu-Fe dual-site enhance the adsorption of NO<sub>3</sub><sup>-</sup> and \*H, thereby improving the reaction kinetics of the NitRR under ambient conditions. However, clarifying the underlying mechanism through more detailed and direct in-situ experimental studies is the key direction for future work. Moreover, the zinc-nitrate battery equipped with the CuO-Fe<sub>3</sub>O<sub>4</sub>/CNTs cathode can simultaneously achieve power generation and ammonia production, with a power density of 11.21 mW cm<sup>-2</sup> and a high Faradaic efficiency of ammonia of 95.4% in 20 mA cm<sup>-2</sup>. These results highlight the crucial role of electrochemical reconfiguration and the synergistic effect between CuO and Fe<sub>3</sub>O<sub>4</sub>, providing an effective strategy for the rational design of high-performance electrocatalysts for nitrate reduction.

### Author contributions:

**Shun Zhang:** Conceptualization, Investigation, Visualization, Writing—original draft. **Shengbo Zhang:** Data curation, Resources, Writing—review & editing. **Jiafang Liu:** Investigation, Resources. **Zhixian Mao:** Investigation. **Yunxia Zhang:** Supervision. **Guozhong Wang:** Supervision. **Huajie Yin:** Supervision. **Haiming Zhang:** Funding acquisition, Supervision, Resources, Writing—review & editing.

### Data Availability Statement

The data supporting this article have been included as part of the Supplementary Information.

### Conflicts of interest

There are no conflicts to declare.

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