nature portfolio

Peer Review File

Isolating Cu-Zn active-sites in Ordered Intermetallics to Enhance Nitrite-to-Ammonia Electroreduction

REVIEWER COMMENTS

Reviewer #1 (Remarks to the Author):

This manuscript reports a nanoporous intermetallic single-atom alloy CuZn (np/ISAA-CuZn) catalyst with completely isolated Cu-Zn active-sites, which achieves ultra-high nitrite reduction to ammonia activity in a neutral environment. A series of in situ experimental studies combined with density functional theory calculations have investigated the reaction mechanism. The catalyst synthesis method is novel, the mechanism is well studied, and the electrocatalytic performance is excellent with realistic application potential. Overall, this is a high-quality manuscript with well-structured, well-organised and well-discussed. Therefore, after addressing the following minor issues, I consider this interesting manuscript suitable for publication in Nature Communications.

1. The authors should have strengthened the informative annotations of the figure notes, e.g. Supplementary Fig. 2. In addition, no obvious Zn oxidation peaks were found in Supplementary Fig. 2, which the authors should have explained.
2. Most of the current research reports on the electrochemical reduction of NOx to ammonia use KOH or K2SO4 as the electrolyte, why did the authors use KHCO3 as the electrolyte?
3. At lower or higher nitrite concentrations, does np/ISAA-CuZn maintain the same level of NO2RR activity?
4. As shown in Fig. S21a, the main peak located near 43° in the XRD pattern of np/ISAA-CuZn after MEA testing seems to contain two peaks, which should be explained by the authors.
5. There are some errors in the manuscript. The author should have checked the manuscript carefully. Such as line 168 “0.2 K KHCO3”, line 320 “np/Cu5Zn8”, etc.
6. The resolution of the images in the manuscript is too low for the reader and should be improved by the author.

Reviewer #2 (Remarks to the Author):

Lan et al. reported a study by isolating Cu-Zn active sites in ordered intermetallics to enhance nitrite-to-ammonia electroreduction. They achieves neutral nitrite reduction reaction with a ammonia Faradaic efficiency over 95% and the high energy efficiency of ≈59.1% in wide potential range from -0.2 to -0.8 V vs. RHE. A series of in situ experimental studies combined with density functional theory calculations, the authors claim that strong electronic interactions of isolated Cu-Zn active-sites altered the protonation adsorption species, effectively alleviating the protonation barrier of *NO2. The reviewer has the following concerns and comments:

1. Nitrite is negatively charged ion in principle. However, at the reducing potentials, the electrode is negatively charged too. The charge repulsion will make its stability low or high energy. In other words, the isolated nitrite should be not present with a high concentration at the surfaces of electrodes. As there are high concentration of proton at the Helmholtz layer, the nitrite should be present in the form of HNO2 molecule. Hence, the authors consider direct NO2* adsorption is not reasonable. It will become

more and more difficult at negative potentials.

2. As the nitrite approaches the interface, it can be captured by proton and concerted with dissociative adsorption at the surface of electrode. In other words, the H+ + NO2- to NO* and OH* is highly possible. These mechanism is not considered in the present mechanism study.

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4. For NOH* protonation and dehydration needs a scission of N-O bond. Its barriers can be high and varying at different potentials. The authors should study the potential-dependent barriers to understand why the ammonia Faradaic efficiency is high from -0.2 to -0.8V vs RHE.

5. Why NO and H2 was not detected in the present experiments? As Cu and Zn are both less reactive elements, the binding of NO is not very strong compared to other transition metals. It is suggested to build up a microkinetic model to study the FEs for NO, H2, NH3 and NH2OH. At -0.8 V vs RHE, the HER should be obverved too.

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8. The reviewer did not find the abbreviation of IMCs. What is "potential barriers"? The authors should use scientific and accurate terminology.

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11. As the performance of nitrite reduction is highly sensitive to the concentration of nitrite, how the electrochemical performance response to the concentration variation?

Reviewer #3 (Remarks to the Author):

In this manuscript by Lan and Tan et. al., nanoporous ordered intermetallic Cu-Zn catalysts are synthesized for the electrochemical nitrite reduction reaction (NO2RR). Overall, the conclusions from the data are defensible. The atomically precise synthesis of the intermetallic catalyst, and its electrochemical performance of 500 mA/cm2 with FE(NH3) ~ 80% for > 1 week operation, are noteworthy results of the manuscript that will be of significance to the electrocatalysis/NOxRR literature and merit publication in Nature Communications. Before publication, some minor revisions should be addressed by the authors.

Introduction

- The reviewer agrees that nitrite is a water pollutant and that there is opportunity to couple water treatment with chemical manufacturing by synthesizing ammonia from nitrite. However, the mass of nitrite pollution worldwide is much less than ammonia demand. Meanwhile, nitrate is a much more prevalent water pollutant that can also be electrochemically reduced to ammonia. In light of this, the reviewer suggests that the authors also frame their work from the fundamental perspective of how studies on NO2RR can inform studies on NO3RR, the latter reaction having more potential to synthesize large amounts of ammonia due to nitrate's greater prevalence in wastewaters.

Results

- How do the electrochemically active surface areas (ECSA) of the 4 catalysts (np/CuZn4, np/Cu5Zn8, np/ISAA-CuZn and np/Cu) compare? Do the ratios of Cu to Zn in the synthesis impact the ECSA of the material, which may impact the electrochemical performance?
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Methods

- Please provide more specifications for the arc-melting
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Responses to the Referees' Comments

We would like to thank all the referees for the careful review and the valuable comments. We have carefully considered the referees' comments and revised the manuscript accordingly. Below we list the changes we have made in light of the referees' comments.

Reviewer #1 (Remarks to the Author):

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Reply: We appreciate the reviewer for recognizing the originality and importance of our work. We also thank the reviewer for the deep and professional comments and suggestions, which are very valuable for improving the scientific impact of this work. By following the reviewer's comments and suggestions, we explained and described in detail. The details will be described below.

1. The authors should have strengthened the informative annotations of the figure notes, e.g. Supplementary Fig. 2. In addition, no obvious Zn oxidation peaks were found in

Supplementary Fig. 2, which the authors should have explained.

Reply: We sincerely thank you for the insightful comments. As shown in **Figure R1**, we have further enhanced the informative annotation (**Supplementary Figure 2** in the revised manuscript). Moreover, the oxidation peaks are weak due to the low ratio of Zn single-phase content in the $Cu_{15}Zn_{85}$ ribbons ($CuZn_5$: Zn = 9:1 at%) (**Figure R1**). In the inset in **Figure R1**, we could note the presence of a distinct Zn oxidation peak.

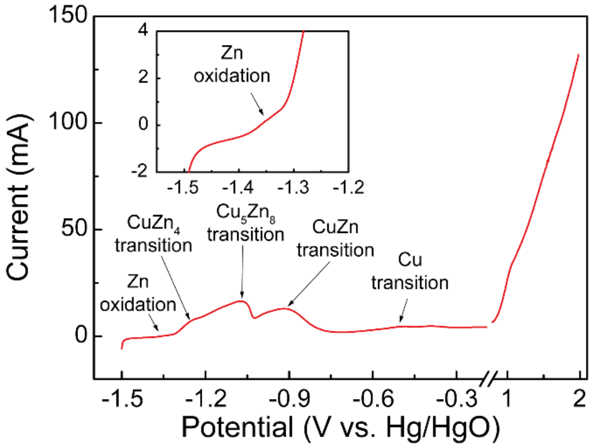

Figure R1. The LSV curve of the $Cu_{15}Zn_{85}$ ribbons in 1 M KOH.

2. Most of the current research reports on the electrochemical reduction of NO_x to ammonia use KOH or K_2SO_4 as the electrolyte, why did the authors use $KHCO_3$ as the electrolyte?

Reply: We sincerely thank you for the insightful comments. It is well known that zinc is an amphoteric metal that reacts with acids and bases, so it may be unstable in strong acid and base electrolytes. Therefore, we chose neutral or near-neutral electrolytes to ensure high stability of the catalysts during the reaction. Moreover, we further tested the NO_2RR performance of np in 0.2 M K_2SO_4 + 10 Mm KNO_2 solution. As show in **Figure R2**, the ammonia FE was 95.9 % and the YR reached 6.34 mg h^{-1} g^{-1} at -0.7 V vs. RHE. However, it could not achieve the high selectivity for ammonia synthesis under a wide potential condition.

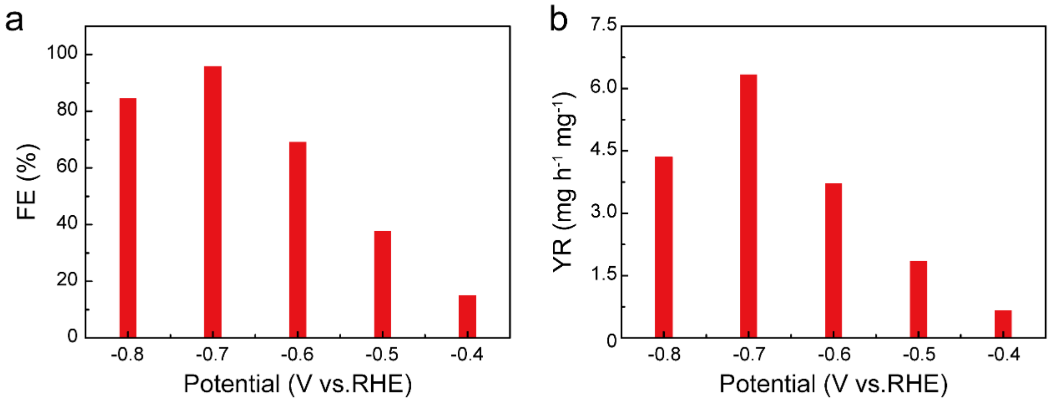

Figure R2. The NH_3 FE (**a**) and YR (**b**) of np/ISAA-CuZn at -0.2 - -0.8 V vs. RHE in 0.2 M K_2SO_4 + 10 mM KNO_2.

3. At lower or higher nitrite concentrations, does np/ISAA-CuZn maintain the same level of NO_2RR activity?

Reply: We appreciate you for this insightful comment. For this comment, we evaluated the performance properties of np/ISAA-CuZn at different nitrite concentrations (page 10, line 7-10, **Supplementary Fig. 22** in the revised manuscript). As shown in **Figure R3**, np/ISAA-CuZn exhibited excellent NH_3 FE (over 90%) range from 1 mM to 1 M NO_2^- concentration, and the ammonia yield increases significantly with increasing nitrite concentration. However, the FE of NH_3 production decreased significantly when the NO_2^- concentration was below 1 mM, probably due to the increased contribution of competitive HER.

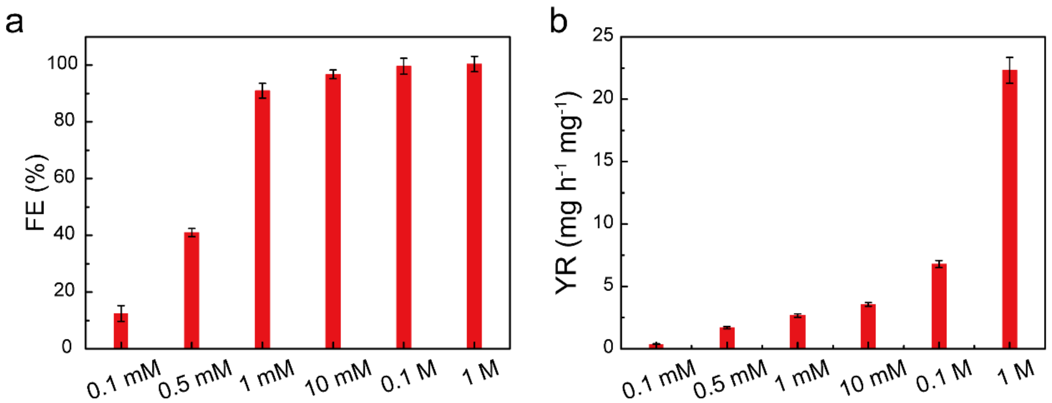

Figure R3. The dependance of NH_3 FE (**a**) and YR (**b**) with respect to NO_2^- concentrations.

4. As shown in Fig. S21a, the main peak located near 43° in the XRD pattern of np/ISAA-CuZn after MEA testing seems to contain two peaks, which should be explained by the authors.

Reply: We appreciate you for the constructive comment and suggestion. The split peaks in the main peak near 43° in the XRD pattern may be due to systematic errors in the testing process. For this comment, as shown in **Figure R3**, we re-examined the XRD of np/ISAA-CuZn after the MEA test, and the diffraction peaks did not show any peak splitting (**Supplementary Fig. 24a** in the revised manuscript).

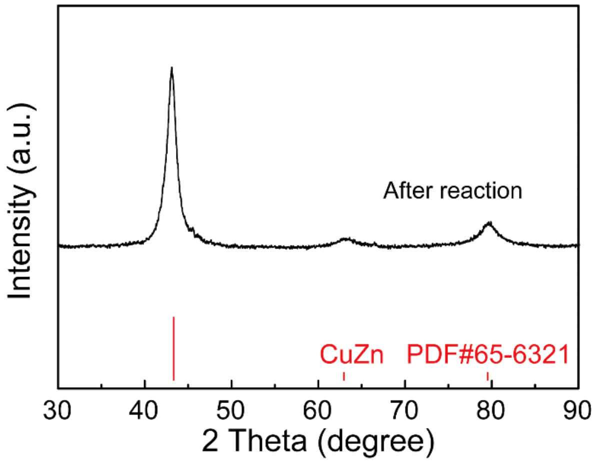

Figure R4. The composition of np/ISAA-CuZn after MEA test.

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manuscript carefully. Such as line 168 “0.2 K $KHCO_3$”, line 320 “np/Cu_5Zn_8”, etc.

Reply: Thank you for reading our paper carefully and pointing out our mistakes. We have corrected the relevant errors in the revised manuscript.

6. The resolution of the images in the manuscript is too low for the reader and should be improved by the author.

Reply: Thank you for the helpful suggestions. We updated all images and increased the resolution of the images.

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Reply: We appreciate the reviewer for recognizing of our work. We also thank the reviewer for the deep and professional comments and suggestions, which are very valuable for improving the scientific impact of this work. By following the reviewer’s comments and suggestions, we have conducted additional experiments and analyses. The details will be described below.

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electrode is negatively charged too. The charge repulsion will make its stability low or high energy. In other words, the isolated nitrite should be not present with a high concentration at the surfaces of electrodes. As there are high concentration of proton at the Helmholtz layer, the nitrite should be present in the form of HNO_2 molecule. Hence, the authors consider direct NO_2* adsorption is not reasonable. It will become more and more difficult at negative potentials.

Reply: We appreciate you for this insightful comment. We could agree more with you on the fact that the presence of the Helmholtz layer may indeed influence reactant adsorption (*J. Phys. Chem. Lett.* **12**, 6988-6995 (2021), *J. Phys. Chem. Lett.* **14**, 685-693 (2023), *Nat. Commun.* **14**, 112 (2023)). It has been shown that when an electrode is immersed in neutral/alkaline electrolyte, an electric double layer is constructed at the electrode-electrolyte interface, where covalently bonded species and reaction intermediates are present in the inner Helmholtz plane (IHP), and hydrated ions are situated in the outer Helmholtz plane (OHP), held by electrostatic force (Chem. Soc. Rev., 2020, 49, 6632-6665, *Proc. Natl. Acad. Sci. USA* **120**, *Nat. Catal.* **2**, 448-456 (2019)). However, as shown in the **Figure R5**, the in situ ATR-SEIRAS test results showed that a distinct $*NO_2$ adsorption peak was detected at ~1211 cm^{-1}. Therefore, we speculate that NO_2^- adsorption does exist during the reaction process. Thus, we did not take the Helmholtz layer into account during the DFT theoretical calculations. Thank you very much for your understanding. Inspired by the aspect, we are more than happy to investigate this in depth in our subsequent research work.

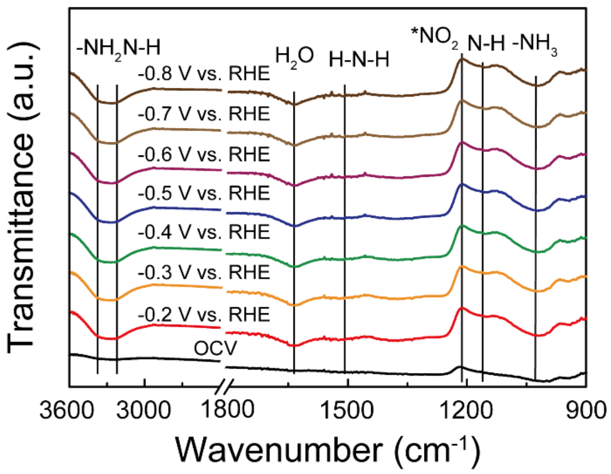

Figure R5. In situ ATR-SEIRAS spectra of the np/ISAA-CuZn in 0.2 M $KHCO_3$ + 10 mM KNO_2.

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Reply: We appreciate you for this insightful comment. We strongly agree with you that the presence of the Helmholtz layer does affect the adsorption of reactants (*J. Phys. Chem. Lett.* **12**, 6988-6995 (2021), *J. Phys. Chem. Lett.* **14**, 685-693 (2023), *Nat. Commun.* **14**, 112 (2023), we added in Ref. 12). It has been shown that in neutral or alkaline environments, the Helmholtz layer does not exist as H^+ but more as hydrated ions or (*Proc. Natl. USA* **120**, e2209979120(2022), *Nat. Catal.* **2**, 448-456 (2019), *Nat Energy* **6**, 1026-1034 (2021)). Thus, what happens in the Helmholtz layer may not be a simple NO_2^- protonation process. Therefore, the pathway of $H^+ + NO_2^-$ conversion to NO* and OH* may not be considered at the moment. However, we agree with you about the influence of the Helmholtz layer on NO_2^- adsorption and subsequent reaction processes. We would be more than happy to investigate this in depth in subsequent research work.

3. All these processes occured at a reducing potential at the electrochemical interface. The electric field and negatively charged surfaces will affect adsorption energies and reaction energies. The authors did not consider all these factors.

Reply: We appreciate the careful consideration of the reviewers. We agree the fact that the electric field and negatively charged surfaces may affect adsorption energies and reaction energies. As fact, it has been shown that the interaction between the electric field and the dipole moment of the adsorbed species has little effect on the free energy (*Phys. Chem. Chem. Phys.* **14**, 1235-1245 (2012)). Moreover, they are much smaller than the typical error estimates from DFT/GGA calculations and thus are unlikely to change the trend studied here. Therefore, we have neglected these effects in this manuscript. Thank you for your understanding.

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Reply: We sincerely thank you for this comment. We have completed the potential-dependent free energy step diagram using the following equation:

$$\Delta G = \Delta E_{DFT} + \Delta E_{ZPE} - T\Delta S - neU$$

The effect of an applied bias, U, is included for all electrode reactions involving an electron by shifting the free energy by $-neU$, where n is the number of electrons.

As shown in **Figure R6**, we found that the barrier for protonation of $*NO_2$ to $*HNOO$ (0.18 eV) is greater than that of $*NOH$ to $*N$ (0.01 eV) for the path of NO_2RR to NH_3 with CuZn catalyst at a standard hydrogen electrode and no voltage applied. This suggests that the rate-determining step for NO_2RR to NH_3 may be in the protonation of NO_2, which is consistent with previous literature (*ACS Catal.* **10**, 494-509 (2020), *Nano Res.* **15**, 972-977 (2022)). When applying a bias voltage of -0.2 V, we found that the protonation process of $*NO_2$ is easier, which is consistent with the high Faraday efficiency of NH_3 obtained in our experiment at -0.2 V. As the bias voltage increases, the entire path also becomes a process of reducing free energy.

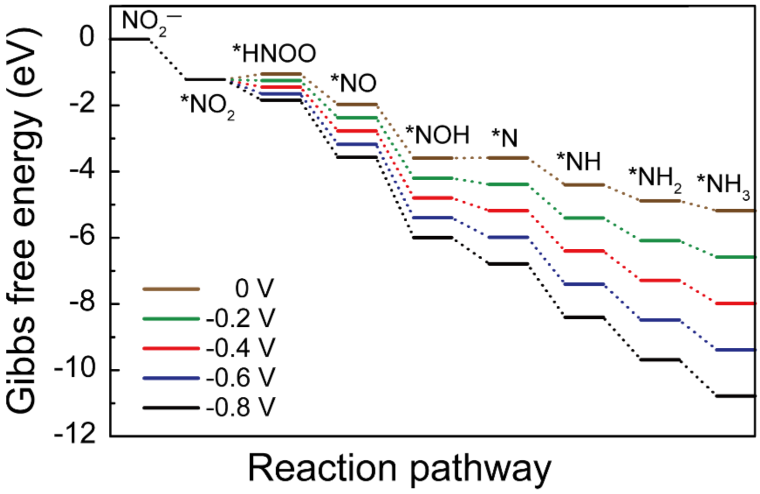

Figure R6. The potential-dependent free energy step diagram.

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Reply: We thank you for the helpful comments. Firstly, we have examined the H_2 and N_2 in the gaseous products using gas chromatography. **Figure R7** shows the H_2 and N_2

FE of np/ISAA-CuZn in 0.2 M $KHCO_3$ + 10 mM KNO_2 solution under different potential conditions, which confirms that the NO_2RR reaction produces small amounts of H_2 and N_2.

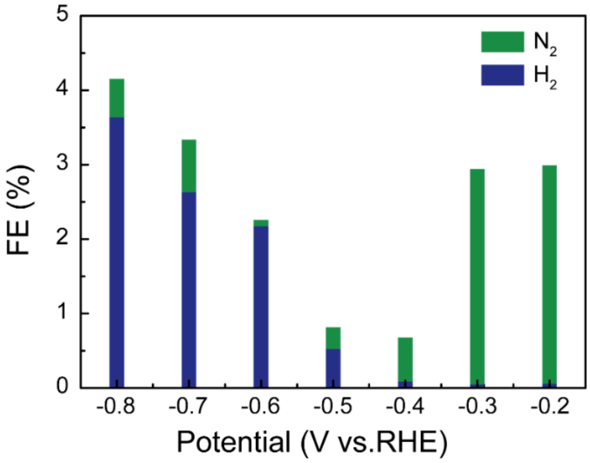

Figure R7. The H_2 and N_2 FE of np/ISAA-CuZn at -0.2 - -0.8 V vs. RHE in 0.2 M $KHCO_3$ + 10 mM KNO_2.

Unfortunately, due to limited experimental conditions, there was a lack of NO standard gas to calibrate the NO peak. For this reason, we investigated different reaction pathways by DFT calculations. As shown in **Figure R8**, the CuZn catalyst surface is more likely to form NH_3 via the NOH pathway than the NO and HNO pathways, and it is difficult to form NO gas.

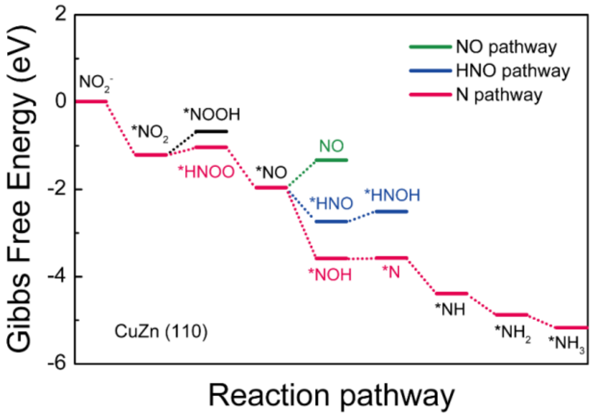

Figure R8. The reaction Gibbs free energy diagrams for NO_2RR on CuZn with three possible pathways.

6. All computations are taken over terrace models. If the more reactive stepped facets were considered?

Reply: We thank you for your insightful comments. We agree with your point of view. It has been shown that stepped surfaces can exhibit higher electrocatalytic performance (*Nat. Commun.* **10**, 2877 (2019), *Nat. Synth.* **2**, 612-623 (2023), *Chem. Soc. Rev.* **43**, 5183-5191 (2014)). Furthermore, according to the characterization results of our catalysts, the existence of stepped surfaces is also reflected (*Nature Mater.* **11**, 775-780 (2012)). However, this manuscript focuses on the effect of crystal structures of different intermetallic phases on the reactivity of NO_2RR. Therefore, the stepped surfaces are not considered in this manuscript. We would be happy to investigate the step surfaces in more detail in future work. Thank you for your understanding.

7. In computational details, the reviewer did not find any descriptions for the solvation effects. How the solvation effects are considered?

Reply: We thank for the reviewer's thoughtful concern. The solvation effect can be considered by adding a correction term of adsorption energy. The reaction free energies (ΔG) were calculated using computational hydrogen model (CHE) as following

$$\Delta G = \Delta E_{DFT} + \Delta E_{ZPE} - T\Delta S + \Delta E_{sol}$$

In equation, the ΔE_{ZPE} is the electronic energy difference between reactants and products obtained via DFT calculations directly. ΔE_{ZPE} and ΔS are the difference in zero-point energy and entropy, respectively. ΔE_{sol} represent the solvation correlation.

For the intermediates, the solvation energies (E_{sol}) were employed from previous reports. (*J. Phys. Chem. Lett.* **12**, 6988-6995 (2021), *ACS Catal.* **10**, 9320-9327 (2020), *Angew. Chem. In. Ed.* **54**, 8255-8258 (2015)):

Table R1. Solubility energy of the intermediates.

Species	Solvation energies (eV)
N*	-0.10
NH*	-0.30
NH_2*	-0.24
NOH*	-0.31
HNO*	-0.23
NO*	-0.03
O*	-0.07
H*	0.01

However, the correction value for this effect is very close to the error value calculated by DFT, and we do not expect this to affect relative adsorption energies of NO_3RR/NO_2RR intermediates on different sites. Therefore, we believe that the solvation effect will not alter the observed DFT trends and correlations.

8. The reviewer did not find the abbreviation of IMCs. What is "potential barriers"? The authors should use scientific and accurate terminology.

Reply: We sincerely thank you for this comment. We have carefully checked the manuscript and revised relevant issues.

9. The authors emphasize the selectivity of nitrite reduction to ammonia is a challenge

issue. This is not true! In fact, the high ammonia selectivity has been realized in many experiments. The real issue for NO_x reduction to ammonia is the high overpotential (-0.8 - 0.7 = -1.5 V vs RHE). Even for -0.2 V vs RHE, the overpotential is still -0.9 V vs RHE.

Reply: We thank you for your insightful comments. As you mentioned, excessive overpotential is indeed a major challenge in NO_x reduction to ammonia. Achieving efficient NO_x reduction to ammonia at low overpotentials is also a goal that we have been pursuing, but the results of the current study are not satisfactory. I hope that a breakthrough can be achieved in our future work. In addition to the high overpotential, the electrochemical conversion of NO_2^- to NH_3 may produce some by-products (NO, N_2H_4, N_2 and H_2) due to complex six-electron transfer reactions. Most of the currently reported catalysts exhibit high ammonia Faraday efficiencies and yields at high nitrite concentrations (>100 mmol L^{-1}). (*Adv. Funct. Mater.* **34**, 2308072 (2024), *Chem. Commun.* **59**, 1625-1628 (2023)). However, efficient electroreduction at low concentrations (≤10 mM) remains a major challenge, mainly due to the restricted migration of reactants near the working electrode and exacerbation of competing hydrogen evolution reactions (*Nat. Commun.* **14**, 7368 (2023)).

10. If the authors have thought about the scale up possibility. In case nitrate, nitrite, and gaseous NO are candidates, if gaseous NO is more friendly for scale up?

Reply: We thank you for your insightful comments. Scale-up has always been our goal, but due to the limitations of the experimental conditions, we are temporarily unable to increase the reaction current density while expanding the electrode area. We also expect to obtain the experimental data with meeting the industrial scale after the experimental equipment is upgraded. Currently, Shao, J. et al. reported a Cu_6Sn_5 electrocatalyst with high activity in the synthesis of ammonia from NO (ammonia production rate of 10 mmol cm^{-2} h^{-1} at current densities greater than 1,400 mA cm^{-2} and Faraday efficiency greater than 96%) (*Nat. Energy* **8**, 1273-1283 (2023), we added in Ref. 20). This work demonstrates the industrial potential of NORR for ammonia synthesis. However, the reduction of gaseous nitrogen oxides to ammonia may face problems such as water insoluble of NO, gas recovery and reuse as compared to nitrates and nitrites. Inspired by these aspects, we would be happy to develope the NORR for ammonia synthesis in future work. Again, we thank the reviewer for recognizing the electro-reduction gaseous NO to NH_3.

11. As the performance of nitrite reduction is highly sensitive to the concentration of nitrite, how the electrochemical performance response to the concentration variation?

Reply: We appreciate you for this insightful comment. For this comment, we evaluated the performance properties of np/ISAA-CuZn at different nitrite concentrations (page 10, line 7-10, **Supplementary Fig. 22** in the revised manuscript). As shown in **Figure R3**, np/ISAA-CuZn exhibited excellent NH_3 FE (over 90%) range from 1 mM to 1 M NO_2^- concentration, and the ammonia yield increases significantly with increasing nitrite concentration. However, the FE of NH_3 production decreased significantly when the NO_2^- concentration was below 1 mM, probably due to the increased contribution of competitive HER.

Reviewer #3 (Remarks to the Author):

In this manuscript by Lan and Tan et. al., nanoporous ordered intermetallic Cu-Zn catalysts are synthesized for the electrochemical nitrite reduction reaction (NO_2RR). Overall, the conclusions from the data are defensible. The atomically precise synthesis of the intermetallic catalyst, and its electrochemical performance of 500 mA/cm^2 with $FE(NH_3)$ ~ 80% for > 1 week operation, are noteworthy results of the manuscript that will be of significance to the electrocatalysis/NO_xRR literature and merit publication in Nature Communications. Before publication, some minor revisions should be addressed by the authors.

Reply: We appreciate the reviewer for recognizing the originality and importance of our work. We also thank the reviewer for the professional comments and suggestions, which are very valuable for improving the scientific impact of this work. By following the reviewer's comments and suggestions, we carefully revised the manuscript and clarified the reviewer's comments. The details will be described below.

Introduction

- The reviewer agrees that nitrite is a water pollutant and that there is opportunity to couple water treatment with chemical manufacturing by synthesizing ammonia from nitrite. However, the mass of nitrite pollution worldwide is much less than ammonia demand. Meanwhile, nitrate is a much more prevalent water pollutant that can also be electrochemically reduced to ammonia. In light of this, the reviewer suggests that the authors also frame their work from the fundamental perspective of how studies on NO_2RR can inform studies on NO_3RR, the latter reaction having more potential to synthesize large amounts of ammonia due to nitrate's greater prevalence in wastewaters.

Reply: We appreciate you for your recognition of our research direction and constructive comments. NO_x^- are currently deemed as a contaminant that produce harmful algal blooms and phytoplankton via eutrophication on rivers, lakes, and coastal waters. The nature's nitrogen cycle balance has been disrupted by the accumulation of nitrogenous pollutants resulting from the massive release of NO_x^- to the biosphere. Furthermore, health concerns about NO_x^- in drinking water arise because excess intake of toxic NO_2^- can lead to diseases including birth defects, methemoglobinemia, spontaneous abortion, and cancer, etc. Developing effective, economical, and environmentally friendly electrochemical technologies for the conversion of NO_x^- from wastewater into NH_3 and address the "NO_x^- time bomb" is of great significance. The selective transformation of harmful NO_x^- to valuable NH_3 via electrocatalysis is therefore crucial for improving public health, protecting the environment, and restoring the balance of ecological nitrogen cycles (*Chem* **9**, 1-60, (2023)). We will endeavor to carry out further research with your suggestions in mind.

Results

• How do the electrochemically active surface areas (ECSA) of the 4 catalysts (np/$CuZn_4$, np/Cu_5Zn_8, np/ISAA-CuZn and np/Cu) compare? Do the ratios of Cu to Zn in the synthesis impact the ECSA of the material, which may impact the electrochemical performance?

Reply: We appreciate you for this insightful comment. For this comment, we performed electrochemical double layer capacitance (C_{dl}) tests to normalise the partial current densities of NH_3 (page 9, line 9-12, **Supplementary Figure 19** in the revised manuscript). As shown in **Figure R9**, np/ISAA-CuZn possessed the highest intrinsic activity compared to other catalysts. We adjusted the ratio of Cu and Zn in the precursor alloys, which was mainly to ensure that the synthesized intermetallic compounds have similar porosity. This behavior may eliminate the influence of porosity on catalytic performance. As fact, the amount of Zn atoms to be removed for the preparation of np/Cu, np/$CuZn_4$, np/Cu_5Zn_8 and np/ISAA-CuZn were 70, 70, 61, 70 at%, respectively. If the same precursor alloy is used for the preparation of intermetallic compounds, there will be a change in the porosity due to the different percentage of Zn atoms removed, which will lead to a huge difference in ECSA.

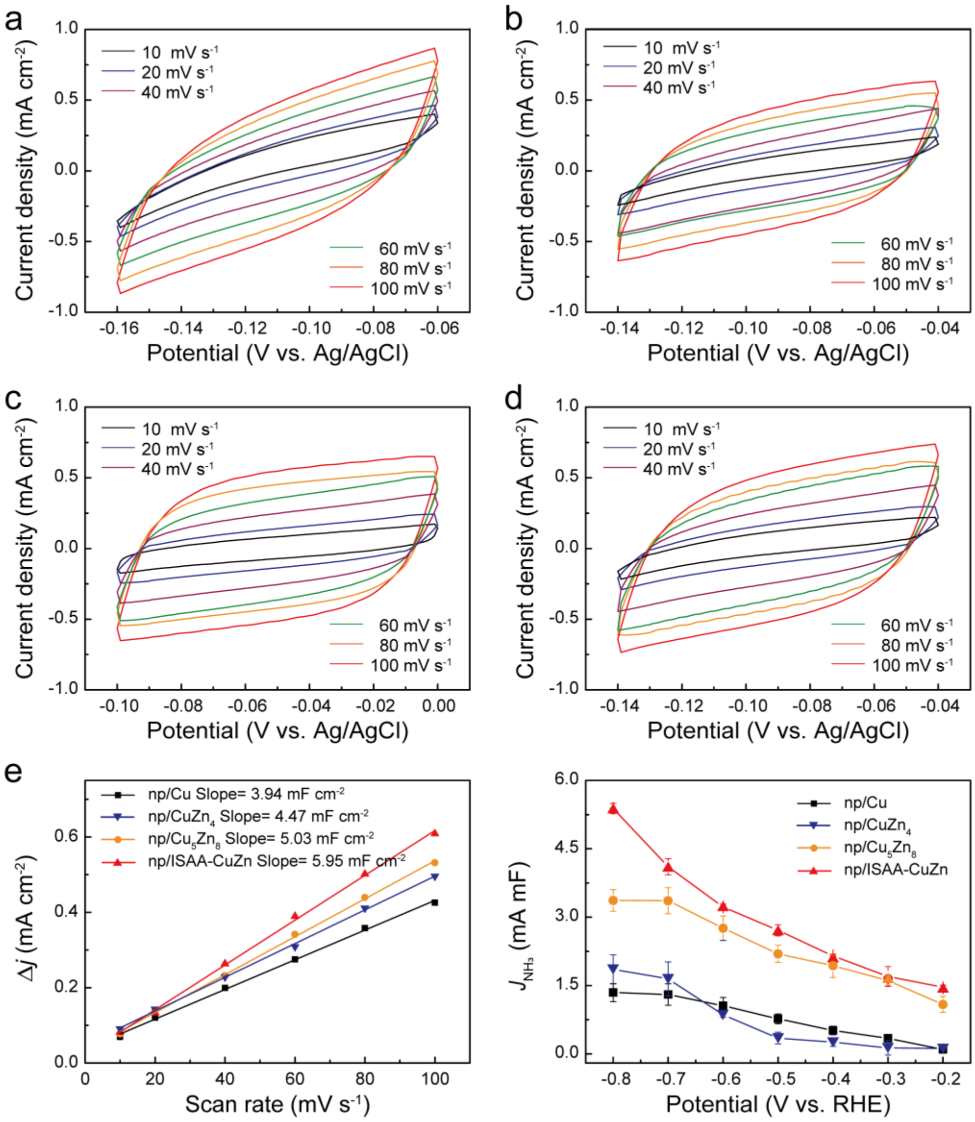

Figure R9. Evaluation of intrinsic activity of different catalysts. Cyclic voltammograms for **a,** np/Cu, and **b,** np/CuZn$_4$, **c,** np/Cu$_5$Zn$_8$, **d,** np/ISAA-CuZn. **e,** Plots of the current density versus the scan rate for np/Cu, np/CuZn$_4$, np/Cu$_5$Zn$_8$ and np/ISAA-CuZn, **f,** ECSA-normalized NH$_3$ current density under different potential of np/Cu, np/CuZn$_4$, np/Cu$_5$Zn$_8$ and np/ISAA-CuZn.

- Where does the remainder of charge go towards in Figure 3g, e.g., were measurements made for hydrogen evolution or other nitrogenous intermediates? Are closed nitrogen mass balances measured across the experiments?

Reply: We appreciate the reviewer for this reminding. For this comment, we examined the gaseous products using gas chromatography. **Figure R10** shows the H_2 and N_2 FE of np/ISAA-CuZn in 0.2 M $KHCO_3$ + 1 mM KNO_2 solution under different potential conditions. The presence of impurities (e.g. N_2) in the carrier gas and the low current density at low potentials interfere with the accurate quantification of N_2. In addition, Unfortunately, due to limited experimental conditions at the moment, there was a lack of NO standard gas to calibrate the NO peak. Thank you for your understanding.

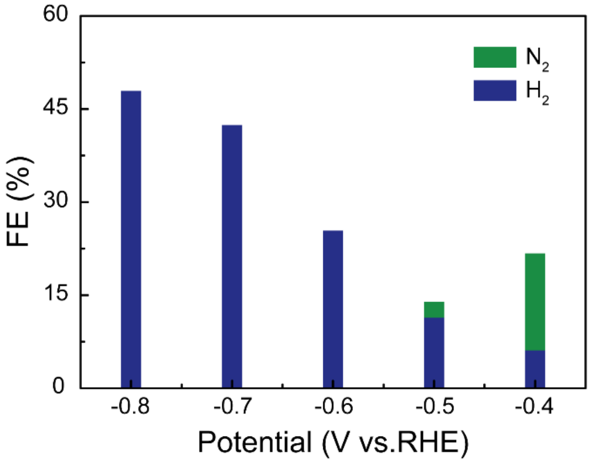

Figure R10. The H_2 and N_2 FE of np/ISAA-CuZn at -0.4 - -0.8 V vs. RHE in 0.2 M $KHCO_3$ + 1 mM KNO_2.

- More details of the MEA electrolysis cell should be given, such as the membrane, electrolyte volumes, flow rates, etc. in order to allow the experiment to be reproduced

Reply: We thank you for the valuable suggestion. For this suggestion, we have included the relevant MEA test details in the manuscript (page 17, line 17-21, in the revised manuscript). The experimental setup used for the MEA electrolysis bath stability tests was a custom MEA electrolysis bath (0.5 cm^2), consisting of a cathodic electrode (np/ISAA-CuZn ribbons), a proton exchange membrane (Nafion117), and an anodic electrode (IrO_2-Ti mesh), with an electrolyte volume of 2.5 L and a flow rate of 10 mL

min^{-1}. We added these details in experiment method.

- Can more explanation be given for how in situ XAS provides enough surface sensitivity for adsorbed nitrite to influence the XANES, e.g., by providing a quick summary from citations 21 and 45. From the reviewer's understanding, XAS (done in fluorescence mode, as the authors report) signal would come from the entire catalyst, and while that may include the surface layer, a majority of the material will not be in contact with nitrite. Could the sensitivity to adsorbed nitrite be related to the geometry of the custom in situ cell, or the porosity of the material? The in situ ATR-SEIRAS and DFT calculations corroborate the facile adsorption of nitrite, which are important observations to support the XAS data.

Reply: We appreciate you for this insightful comment. We strongly agree with your understanding. XAS is a bulk per-atom averaging technique that measures not only the surface-active sites, but also the paracrine portion of the core, and thus the internal core atoms dilute the XAS signal from the surface atoms. This dilution may blur any potential-induced and adsorption-induced changes of the spectra and introduce considerable uncertainty to determine the structural parameters of adsorbed species. The key to solving this challenge is to increase the surface-to-volume ratio to obtain a sufficient surface signal, which is also consistent with the general requirements of practical electrocatalysts (*Current Opinion in Electrochemistry* **27**, 100681 (2021)). Nanoporous materials with their unique porous structure can expose many active sites, which can effectively increase the surface-to-volume ratio. Therefore, we speculate that microstructural design may be an effective way to efficiently improve surface sensitivity. Nanoporous materials with their unique porous structure can expose many active sites, which can effectively increase the surface-to-volume ratio and thus obtain accessible XAS signals (*ACS Energy Lett.* **5**, 192-199 (2020), *Adv. Mater.* **33**, 2007733 (2021)). Thus, we believe that np/ISAA-CuZn can adsorb nitrite providing sufficient surface sensitivity to obtain reliable in situ XAS data. However, the data sensitivity is still low compared to that of single-atom catalysts, and thus efforts are still needed in the structural design and synthesis of catalysts.

Methods

- Please provide more specifications for the arc-melting

Reply: We thank you for your valuable suggestions. Based on your suggestion, we have added the corresponding specification information for arc-melting (page 15, line 9- 18 in the revised manuscript). The pure Cu (99.9999%, Beijing Jiaming Platinum Nonferrous Metals Co., Ltd.) and pure Zn (99.995%, Beijing Jiaming Platinum Nonferrous Metals Co., Ltd.) were mixed in a certain ratio (The atomic percentages of Cu and Zn in the precursor alloys of np/$CuZn_4$, np/Cu_5Zn_8, np/ISAA-CuZn, and np/Cu were 6: 94, 15: 85, 15: 85 and 30: 70, respectively) and arc-melted (Ar atmosphere, 99.999%, Changsha Gaoke Gas Co.) to prepare Cu-Zn alloy ingots. The size of the precursor alloy ingot prepared by arc melting is φ10 mm × 8 mm. Subsequently, melt spinning technology was introduced to remelt the alloy ingot and quickly quenched on the surface of the spinning Cu roll at a rotation speed of 2 K rpm. Ribbons with dimensions ~30 μm thick, ~2 mm wide, and ~10 cm long were achieved.

• Please provide more information about the electrochemical system and amperometry (np/$CuZn_5$ at dealloying voltage of 1.26 V vs. Hg/HgO). For example, what does "based on the steady-state current vs. voltage diagram" mean in the context of what experimental decisions were made? How long was the applied potential held for? How was the material made/used into a working electrode? What area of electrode was exposed to electrolyte and how (electrode holder, compression with a narrow area exposed, etc)?

Reply: We thank you for your constructive comments. Firstly, we apologize for the misunderstandings and misrepresentation of details caused by our inappropriate descriptions. Therefore, we have adjusted and corrected the details of the material synthesis in the Methods section accordingly (page 15 line 18-22, and page 16 line 1-4 in the revised manuscript). The chronoamperometry curves of np/$CuZn_5$, np/$CuZn_4$, np/Cu_5Zn_8, np/ISAA-CuZn, and np/Cu at the corresponding voltages are shown in **Figure R11**. The electrochemical dealloying potentials of np/$CuZn_5$, np/$CuZn_4$, np/Cu_5Zn_8, np/ISAA-CuZn, and np/Cu were -1.32V, -1.26 V, -1.15 V, -0.95 V, and -0.50 V vs. Hg/HgO, and the corresponding dealloying time are ~6.0 h, ~3.2 h, ~4.0 h, ~3.0 h and ~1.3 h, respectively (the duration of dealloying may vary depending on the size of the precursor alloy strip). The electrodes were prepared as follows (page 16, line 1, and page 17, line 1-5 in the revised manuscript): 10 mg of catalyst was ultrasonically dispersed in 1 mL of a solution (40 μL of Nafion solution (RG, 5 wt%,Adamas), 960 μL of ethanol, and ultrasonicated for 30 mins to form a uniform ink. 40 μL (~0.4 mg) of a uniform ink dispersion was taken with a pipette, loaded onto the gas diffusion layer

(1×1 cm^2, Sigraset 29 BC) electrode, and dried under ambient conditions, with an area of 1 cm^2 of the electrode exposed to the electrolyte.

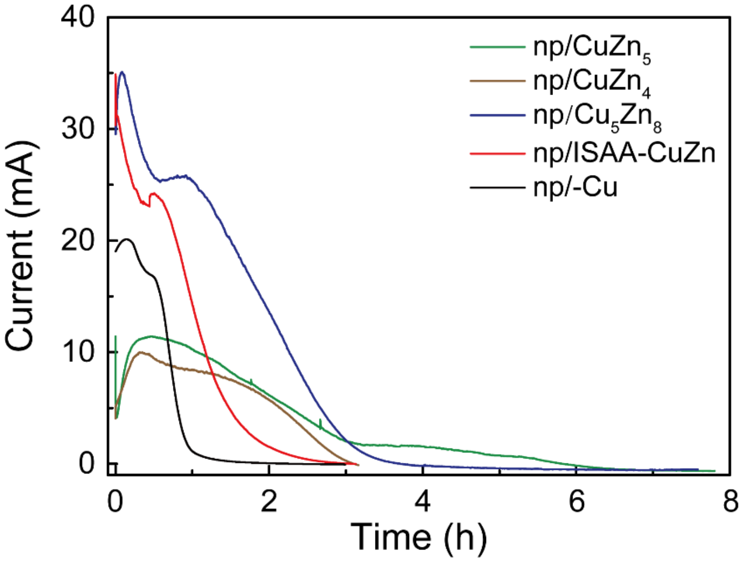

Figure R11. The chronoamperometry curves of np/CuZn$_5$, np/CuZn$_4$, np/Cu$_5$Zn$_8$, np/ISAA-CuZn, and np/Cu at the corresponding voltages.

- How was a catalyst loading of ~ 0.4 mg/cm^2 estimated? A methodology / calculation should be given?

Reply: We sincerely thank you for this comment. The electrodes were prepared as follows (page 16, line 1, and page 17, line 1-5 in the revised manuscript): 10 mg of catalyst was ultrasonically dispersed in 1 mL of a solution (40 μL of Nafion solution (RG, 5 wt%,Adamas), 960 μL of ethanol, and ultrasonicated for 30 mins to form a uniform ink. 40 μL (~0.4 mg) of a uniform ink dispersion was taken with a pipette, loaded onto the gas diffusion layer (1×1 cm^2, Sigraset 29 BC) electrode, and dried under ambient conditions. The loading of catalyst for the resulting electrode was ~0.4 mg cm^{-2}.

- Can schematics and/or pictures of the in situ cells be provided to increase reproducibility of the experiments / give the reader a greater understanding of how the measurement was taken?

Reply: We appreciate you for this insightful suggestion. As shown in **Figure R12**, we have added corresponding optical photograph of the in situ XAS (**Supplementary Figure 25** in the revised manuscript) and in situ ATR-SEIRAS (**Supplementary Figure 27** in the revised manuscript) electrolysis cells.

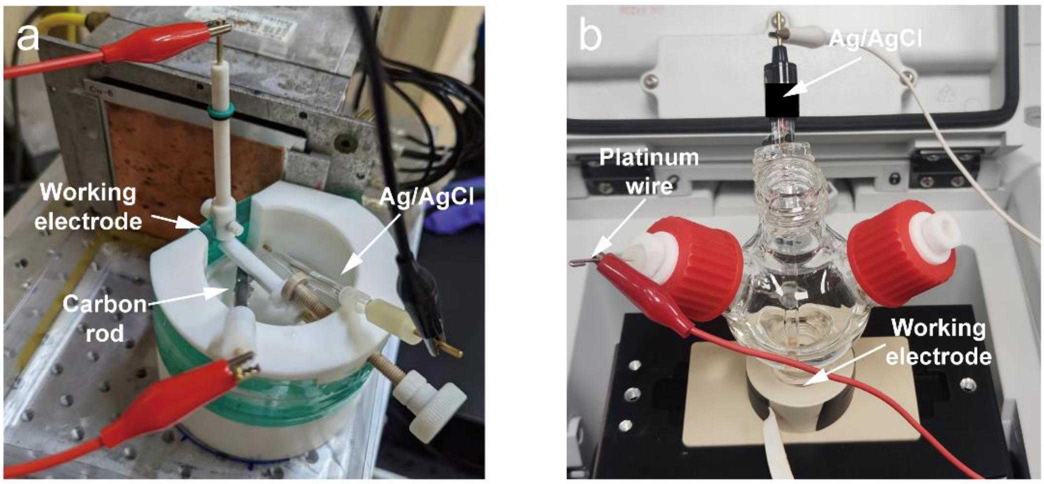

Figure R12. Optical photographs of the custom electrolysis cells used for in situ XAS (**a**) and in situ ATR-SEIRAS (**b**).

General comments

The manuscript needs to be proofread for grammatical mistakes / typos before acceptance. There are many throughout, such as:

- Line 107: "dissolved" is in the wrong tense
- Lines 43-44: "rationally designed of advanced electrocatalysts...?
- Line 94: "the precisely synthesis of..."
- Line 168: "0.2 K $KHCO_3$"

- Line 170: "absentce of NO_2^-"

- Line 252: should be "three", not "there"

Reply: We thank the reviewers for carefully reading our paper and pointing out our errors. We have corrected related errors in the revised manuscript.

REVIEWER COMMENTS

Reviewer #1 (Remarks to the Author):

The manuscript is OK for acceptance.

Reviewer #2 (Remarks to the Author):

Comment 1: The NO2* signals can not be used as evidence to conclude the nitrite was directly adsorbed on the surfaces. The authors did not really respond to my concern that the negatively charged nitrite must be repulsive to the surface of electrodes.

Comment 2: The cation is rich at the Helmholtz layer that the nitrite + cation can be really a concerted pair to dissociate N-O bond. The authors should strictly calculate these processes.

Comment 7: The authors did not cite these references of solvation energies in the main texts. It is suggested to add a few descriptions of the computational details and important references in the main texts.

Reviewer #3 (Remarks to the Author):

The authors have done a good job addressing my previous suggestions. I appreciate that they measured ECSA, reported FEs to H2 and N2 production, and provided more experimental details in general. I suggest the authors please include their response on increased surface area:volume as being an important parameter for surface-sensitivity in XAS, as they detailed in the response to reviewers. For example, the following statement should be included in the manuscript: "the data sensitivity is still low compared to that of single-atom catalysts, and thus efforts are still needed in the structural design and synthesis of catalysts". The ECSA and FE data should be included in the SI as well. With these additional incorporations, I believe the manuscript should be published.

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The manuscript is OK for acceptance.

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Responses to the Referees' Comments

We would like to thank all the referees for the careful review and the valuable comments. We have carefully considered the referees' comments and revised the manuscript accordingly. Below we list the changes we have made in light of the referees' comments.

Reviewer #1 (Remarks to the Author):

The manuscript is OK for acceptance.

Reply: We are very grateful to your encouraging and positive comments and really appreciate your agreement of acceptance with this revised manuscript.

Reviewer #2 (Remarks to the Author):

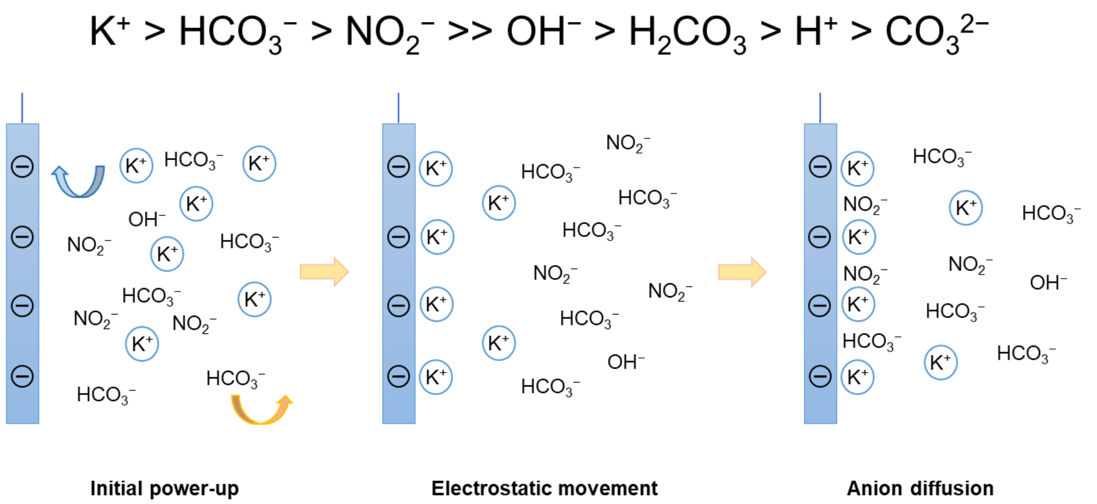
Comment 1: The NO_2* signals can not be used as evidence to conclude the nitrite was directly adsorbed on the surfaces. The authors did not really respond to my concern that the negatively charged nitrite must be repulsive to the surface of electrodes.

Reply: We apologize for not clearly explaining your concerns in our previous response. We are agree that the cathode is usually negatively charged at the reduction potential, leading to enrichment of cations and depletion of anions in the vicinity of the electrode, resulting in the formation of an electrical double layer (EDL) (*ACS Catal.* **12**, 331-362 (2022)). However, when occurring in the vicinity of the electrode, the structure and composition of the EDL becomes more complex, with cations/hydrated cations gradually accumulating in the EDL as a result of Coulombic interactions, thereby increasing the local electrode potential and affecting the kinetic step. Cations in the electrolyte have been shown to dramatically alter the rate and reaction selectivity of many electrocatalytic processes (*J. Chem. Phys.* **151**, 160902 (2019), *Proc. Natl. Acad. Sci. USA* **120**, e2209979120 (2023), *Nat. Commun.* **15**, 616 (2024)). Morevore, the presence of cations relieves the Coulomb repulsion between the nitrate anion and the negatively biased electrode.Therefore, the role of cations should not be overlooked.

Herein, the electrolytes used in our tests were 0.2 M $KHCO_3$ + 10 mM KNO_2 or 0.2 M $KHCO_3$ + 1 mM KNO_2. $KHCO_3$ is a strong electrolyte that dissolves in water and becomes fully ionized, forming K^+ and HCO_3^-. In addition, the hydrolysis of HCO_3^- (producing OH^-) is greater than the ionization (producing H^+), and the ionic concentrations in solution are distributed as follows:

$$K^+ > HCO_3^- > NO_2^- >> OH^- > H_2CO_3 > H^+ > CO_3^{2-}$$

Among them, the concentrations of K^+, HCO_3^-, and NO_2^- ions are much higher than those of OH^- and H^+ ions. When the negative electrode is introduced into the solution, the ions will exhibit the different behaviors as shown in **Scheme 1**. Initially, electrostatic forces result in an enrichment of cations (K^+) and a depletion of anions (HCO_3^-, NO_2^- and very small amounts of OH^-) in the vicinity of the electrode. However, as more and more K^+ ions near the anode surface shield the anode potential, the ion concentration difference begins to dominate and large amounts of NO_2^- and HCO_3^- approach the electrode surface. This may be the main reason for the $^*NO_2$ adsorption peak during the in situ ATR-SEIRAS test. Beyond the effect of cation, other electrolyte factors such as solvents, anions, local pH, impurities, additives, and surface modifiers can also significantly affect the properties of EDL. We will perform more comprehensive and detailed calculations in the follow-up work. Many thanks for your understanding.



Scheme 1. The behavior of ions on the negative electrode surface in $KHCO_3$ and KNO_2 solution.

Comment 2: The cation is rich at the Helmholtz layer that the nitrite + cation can be really a concerted pair to dissociate N-O bond. The authors should strictly calculate these processes.

Reply: We appreciate the careful consideration of the reviewers. According to our testing conditions, there are many K^+ cations in the vicinity of Helmholtz layer, which we had not previously considered. Therefore, we further performed out DFT calculation to investigate the influence of K^+ on the reaction path. As shown in the **Figure R1**, we found that the introduction of K^+ can effectively stabilize the reactant intermediates and reduce their adsorption energy. In addition, the trend of rate-determining step (RDS) did not change after the introduction of K^+, and the RDS energy barriers of CuZn (110) were all lower than those of Cu (111). Due to the limitations of the factors, we have considered so far, we will carry out more comprehensive and detailed calculations about cations and other electrolyte factors, as well as synergistic effects between electrolyte factors in our subsequent work. Thank you very much for your understanding.

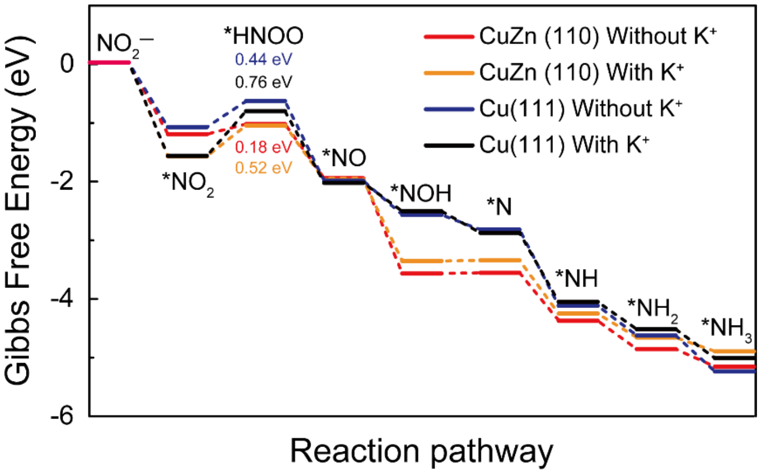


Figure R1. Comparison of reaction paths with and without K^+ on the surface of CuZn (110) and Cu (111).

Comment 7: The authors did not cite these references of solvation energies in the main texts. It is suggested to add a few descriptions of the computational details and important references in the main texts.

Reply: We appreciate your helpful suggestions. Following your suggestion, we have added a description of the solvent energy (page 21, line 11-12) and the corresponding references in the calculation section (*J. Phys. Chem. Lett.* **12**, 6988-6995 (2021), *Angew. Chem. In. Ed.* **54**, 8255-8258 (2015), we added in Ref. 58 and 59). Moreover, for your convenience, we added some clarification in the calculation section (page 22, line 3-10).

page 21: The correction for solvent effects was not considered for the time being as it was very close to the error value calculated by the DFT [58, 59].

58. Long J. et al. Unveiling potential dependence in NO electroreduction to ammonia. *J. Phys. Chem. Lett.* **12**, 6988-6995 (2021).

59. Clayborne, A., Chun, H. -J., Rankin, R. B. & Greeley, J. Elucidation of pathways for NO electroreduction on Pt (111) from first principles. *Angew. Chem. Int. Ed.* **54**, 8255-8258 (2015).

page 22: The zero-point vibrational energies, internal energy and entropies of the adsorbates were computed from vibrational frequency calculations, in which only the adsorbate vibrational modes were computed explicitly, while the catalyst was fixed (*J. Phys. Chem. Lett.*, **12**, 6988-6995 (2021); *ACS Sustainable Chem. Eng.*, **10**, 14343-14350 (2022); *J. Phys. Chem. Lett.* **13**, 9919-9927 (2022); *ACS Catal.* **14**, 4423-4431(2024), we added in Ref. 61-63).

The reaction free energies (ΔG) were calculated using computational hydrogen model (CHE) (*J. Phys. Chem. B* **108**, 17886-17892 (2004), we added in Ref. 64) proposed by Nørskov as following.

$$(H^{+}+e^{-}) \rightarrow \frac{1}{2}H_2$$

61. Yang R., Li H., Long J., Jing H., Fu X., and Xiao J. Potential dependence of ammonia selectivity of electrochemical nitrate reduction on copper oxide. *ACS Sustainable Chem. Eng.* **10**, 14343-14350 (2022).

62. Mou T. et al. Predictive theoretical model for the selective electroreduction of nitrate to ammonia. *J. Phys. Chem. Lett.* **13**, 42, 9919-9927 (2022).

63. Long J. et al. Fundamental insights on the electrochemical nitrogen oxidation over metal oxides. *ACS Catal.* **14**, 4423-4431 (2024).

65. Nørskov, J. K., Rossmeisl, J., Logadottir, A., Lindqvist, L., Kitchin, J. R., Bligaard, T., Jonsson. H. Origin of the overpotential for oxygen reduction at a fuel-cell cathode. *J. Phys. Chem. B* **108**, 17886-17892 (2004).

Reviewer #3 (Remarks to the Author):

The authors have done a good job addressing my previous suggestions. I appreciate that they measured ECSA, reported FEs to H_2 and N_2 production, and provided more experimental details in general. I suggest the authors please include their response on increased surface area: volume as being an important parameter for surface-sensitivity in XAS, as they detailed in the response to reviewers. For example, the following statement should be included in the manuscript: "the data sensitivity is still low compared to that of single-atom catalysts, and thus efforts are still needed in the structural design and synthesis of catalysts". The ECSA and FE data should be included in the SI as well. With these additional incorporations, I believe the manuscript should be published.

Reply: We appreciate your recommendation of acceptance and helpful comments in the reviewing process and are pleased to have our manuscript be reviewed by you. Following your suggestion, we have added the appropriate statement to the revised manuscript (page 12, line 8-12 of the revised manuscript) and added the ECSA (**Supplementary Figure 20** in the revised manuscript) and FE data to the manuscript (**Supplementary Figure 18** and **Supplementary Figure 23** in the revised manuscript).

REVIEWER COMMENTS

Reviewer #2 (Remarks to the Author):

The Comments 1 & 2 are just related with the same issue. At the negative potentials, the electrode surface is highly negatively charged, the concentration of nitrite is very low at the EDL, the direct adsorption is very unlikely, unreasonable. The first step in Fig. 5 will be a very unlikely process. KNO2 (or HNO2) neutral species can be more accurate adsorbates with more high probability.

In a recent conference, an experimentalist asked the same question for nitrate reduction: How and why the negatively charged nitrate can be directly adsorbed on the negatively charged electrode surface? The speaker was not prepared and mute for a long time!!

The Figure R1 is certainly not correct, because your K is not solvated potassium ion and the surface is not properly negatively charged!! Therefore, your additional results can not support your explanations.

The authors must understand that the reviewer is not the barrier of publication! As the work was published, its positive or negative impact is just starting and propagating. I will be not reviewing this manuscript. I have provided all my comments and suggestions and the editor will decide if these are important issue needed revision.

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Responses to the Referees' Comments

We would like to thank all the referees for the careful review and the valuable comments. We have carefully considered the referees' comments and revised the manuscript accordingly. Below we list the changes we have made in light of the referees' comments.

Reviewer #2 (Remarks to the Author):

The Comments 1 & 2 are just related with the same issue. At the negative potentials, the electrode surface is highly negatively charged, the concentration of nitrite is very low at the EDL, the direct adsorption is very unlikely, unreasonable. The first step in Fig. 5 will be a very unlikely process. KNO_2 (or HNO_2) neutral species can be more accurate adsorbates with more high probability.

Reply: We are very grateful for the insights you have provided. We apologize for our failure to fully understand your review. Your suggestions have been a useful aid in our understanding of the NO_2RR reaction mechanism.

As we know, the electrocatalytic reactions occur at the electrode-electrolyte interface. Electrolytes have been considered to highly participate in the electrocatalytic process via their interactions with catalyst surface, reactants, intermediates, and even the products (*ACS Catal.* **12**, 331-362 (2022)). The electrolyte microenvironment is influenced by a variety of factors, including electrolyte concentration, local pH, cation effect, and anion effect. (*ACS Catal.* **12**, 331-362 (2022), *Angew. Chem. Int. Ed.* **63**, e202408382 (2024), *Nat. Catal.* **2**, 198-210 (2019)). For example, Xin-Yao Yu et al. revealed that K^+ can create a most negative electrostatic potential in EDL to accelerate the protons in solution to pass through EDL to the catalyst surface (*Angew. Chem. Int.

Ed. **63**, e202408382 (2024)). Waegele et al. recently discussed the role of cations of electrolyte in affecting the electrical double layer (EDL), as well as the reaction rate and selectivity of electrocatalytic process (*J. Chem. Phys.* **151**, 160902 (2019), *Phys. Chem. Chem. Phys.* **19**, 30166-30172 (2017)).The cations or hydrated cations occupied in EDL were found to block the catalytic active sites, redistribute the local potential drop (the driving force of charge transfer), affect the electric dipole moments and the polarizabilities of adsorbed intermediates in the presence of the interfacial electric field, influence the chemical interactions, change the pH buffer ability, and alter the interfacial water structure. However, Monteiro and co-workers recently precluded the effect of electric field and local pH buffer, instead, partially desolvated metal cations stabilize the CO_2^- intermediate via a short-range electrostatic interaction, which enables its reduction, because they found that CO_2 reduction does not exactly occur in the absence of metal cations (*Nat. Catal.* **4** 654-662 (2021)). It has been reported that local pH increase can inhibit the occurrence of competitive hydrogen evolution reactions, thus favoring the generation of C_2 products during electrocatalytic carbon dioxide reduction (*J. Am. Chem. Soc.* 138, 13006-13012 (2016)). As can be seen, the electrolyte microenvironment can greatly affect the activity, selectivity and Faradaic efficiency of the challenging electrocatalytic reactions. Exploring the effect of EDL on the reactant adsorption process requires a combination of complex electrolyte factors (e.g., cations, solvents, anions, local pH, etc.). Presently, there is little agreement on how to consider the first step mechanism due to the complexity of the EDL [55]. Therefore, we focused on the effect of different Cu-Zn IMCs crystal structures on

NO_2RR activity under similar microenvironment by DFT calculations without considering the EDL at this moment. The reaction mechanism of NOx^-RR has been reported in many works (Chem 9, 1-60 (2023)). However, there is agreement on how to consider the first step mechanism due to the complexity of the EDL. There are mainly two approximations: 1. $* + NO_x^- + H^+ \rightarrow *NO_x^- + (H+ + e^-)$; 2. $* + NO_x^- + H+ \rightarrow *HNO_x$ (ACS Sustainable Chem. Eng. 10, 14343-14350 (2022)). We strongly agree with you that KNO_2 neutral species can be more accurate adsorbents. We consider that the adsorption process may be the co-adsorption of K and NO_2 on the catalyst surface to form $*NO_2$ intermediates (See **Figure 5a**) (page 13 line13-22, and page 14, line 1-5, and page 15, line 11-14). Although our DFT calculations is not considered the influence of the EDL, it still provides an overview of thermodynamics tendency on ISAA-CuZn for the NO_2RR. We believe that the investigation of the EDL effects is crucial for the study of the NO_2RR mechanism at low concentrations of NO_2^-, which will motivate us to investigate by combining experimental results, macroscopic kinetic characterization and DFT calculations with considering the EDL in further work. Thank you for your understanding.

Moreover, we calculated the adsorption and dissociation processes of water on the Cu and ISAA-CuZn surfaces, which provide the necessary *H for the protonation (hydrogenation) step of the $*NO_2$ (page 15, line 14-20). **Figure R1** show that the Zn site favors the adsorption of H_2O molecules and effectively lowered the hydrolysis dissociation barrier (0.28 eV), which provides sufficient protonic hydrogen for the reaction intermediate. This provides an important guarantee that ISAA-CuZn exhibits excellent NO_2RR activity. Moreover, we have carefully revised the manuscript (page 12 line 16-18, and page 13, line 13-16).

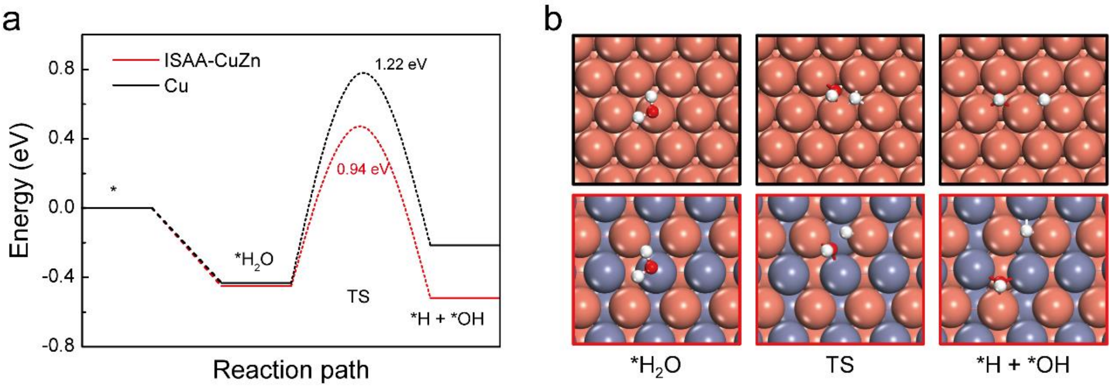

Figure R1. Calculated of the water dissociation step on Cu and ISAA-CuZn surfaces. a, Free energy diagrams, b, the structure of the $*H_2O$, transition state (TS), and *H+ *OH of the reaction process.

page 12: In general, the cathode is usually negatively charged at the reduction potential, leading to cation enrichment and anion depletion near the electrode, resulting in the formation of an electrical double layer (EDL) [53, 54]. When occurring in the vicinity of the electrode, the structure and composition of the EDL becomes more complex. Studying the adsorption process of reactants in EDL requires a combination of complex electrolyte factors (e.g., cations, solvents, anions, local pH, impurities, additives, and surface modifiers). It has been shown that disregarding the effects of volumetric vignettes and bilayers can also provide a correct thermodynamic profile [55]. We focused on the effect of different Cu-Zn IMCs crystal structures on NO_2RR activity by DFT calculations. Currently, there is no consensus on how to consider the first step of the NO_x^- adsorption mechanism due to the complexity of the EDL [56].Recent literatures have shown that there are two main processes regarding reactant adsorption: process 1.

$* + NO_x^- + H^+ \rightarrow *NO_x^- + (H+ + e^-)$; process 2. $* + NO_x^- + H+ \rightarrow *HNO_x$ [56]. Since the experimental solution is neutral, we consider the KNO_2 species as the adsorbent, and the adsorption process could be the co-adsorption of K and NO_2 on the catalyst surface to form $*NO_2$ intermediates (similar to process 1) (**Fig. 5a**).

53 Deng, B., Huang, M., Zhao, X., Mou, S. & Dong, F. Interfacial electrolyte effects on electrocatalytic CO_2 reduction. *ACS Catal.* **12**, 331–362 (2022).

54 Wen, W., Fang, S., Zhou, Y., Zhao, Y., Li, P., and Yu X-Y. Modulating the Electrolyte Microenvironment in Electrical Double Layer for Boosting Electrocatalytic Nitrate Reduction to Ammonia. *Angew. Chem. Int. Ed.* ***2024**, 63, e202408382.*

55 Yang Y., Li J., Chen K., Chen Q-j., Feng Y. Catalytic Performance of Two-Dimensional Bismuth Tuned by Defect Engineering for Nitrogen Reduction Reaction. *J. Phys. Chem. C* **124**, 19563-19570 (2020).

56 Yang R., Li H., Long J., Jing H., Fu X., and Xiao J. Potential dependence of ammonia selectivity of electrochemical nitrate reduction on copper oxide. *ACS Sustainable Chem. Eng.* **10**, 14343-14350 (2022).

page 15: We strongly believe that the investigation of the NO_2^- adsorption process is crucial for the study of the NO_2RR reaction mechanism. We will investigate this in depth in our subsequent work by combining experimental results, macroscopic kinetic characterization and DFT calculations.

page 15:Furthermore, we calculated the adsorption and dissociation processes of water on the Cu and ISAA-CuZn surfaces (**Supplementary Fig. 36**), which provide the necessary *H for the protonation (hydrogenation) step of the *NO_2. The results show that the Zn site could effectively lower the hydrolysis dissociation barrier (0.28 eV), which provides sufficient protonic hydrogen for the reaction intermediate. This provides an important guarantee that ISAA-CuZn exhibits excellent NO_2RR activity.

page 23: The calculation of reaction free energy (G) is based on the computational hydrogen model (CHE) proposed by Nørskov as following [63]:

$$(H^{+}+e^{-})\rightarrow\frac{1}{2}H_2$$

Transition states (TS) were located using the climbing-image nudged elastic band (CI-NEB) method with the quasi-Newton algorithm [64].

63. Nørskov, J. K., Rossmeisl, J., Logadottir, A., Lindqvist, L., Kitchin, J. R., Bligaard, T., Jonsson. H. Origin of the overpotential for oxygen reduction at a fuel-cell cathode. *J. Phys. Chem. B* **108**, 17886-17892 (2004).
64. Henkelman, G. et al. A climbing image nudged elastic band method for finding saddle points and minimum energy paths. *J. Chem. Phys.* **113**, 9901-9904 (2000).

In a recent conference, an experimentalist asked the same question for nitrate reduction: How and why the negatively charged nitrate can be directly adsorbed on the negatively charged electrode surface? The speaker was not prepared and mute for a long time!!

Reply: We thank you for your insightful comments. As you say, at present, the NO_2RR/NO_3RR research reports do not go far enough on the reactant adsorption process. This may be due to the fact that studying the adsorption process of reactants in EDL requires a combination of complex electrolyte factors (e.g. cations, solvents, anions, local pH, impurities, additives, and surface modifiers). We look forward to more comprehensive and detailed calculations during subsequent studies. Thank you for your understanding.

The Figure R1 is certainly not correct, because your K is not solvated potassium ion and the surface is not properly negatively charged!! Therefore, your additional results can not support your explanations.

Reply: Thank you very much for your insightful comments. We deeply apologize for our inappropriate findings. Your comment provides us with very valuable suggestions and points us in the right direction for our subsequent studies.

The authors must understand that the reviewer is not the barrier of publication! As the work was published, its positive or negative impact is just starting and propagating. I will be not reviewing this manuscript. I have provided all my comments and suggestions and the editor will decide if these are important issue needed revision.

Reply: Your instructive suggestions are greatly appreciated. We apologize for our previous failure to properly and deeply understand your comments and suggestions. For this reason, we have scrutinized the manuscript to correct some inappropriate descriptions. In addition, we have further investigated the water adsorption and dissociation processes of ISAA-CuZn and Cu. We hope that our efforts have answered your questions and thank you for your understanding.