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Peer Review File

Upgrading of nitrate to hydrazine through cascading electrocatalytic ammonia production with controllable N-N coupling

REVIEWER COMMENTS

Reviewer #1 (Remarks to the Author):

Han et al. demonstrated an innovative approach for upgrading NOx wastes to valuable N2H4 (salts) chemicals through the integration of NOx electroreduction to NH3 and NH3 oxidation to N2H4, employing a ketone mediator to moderate the N-N coupling process. They proposed lattice-oxygen-mediated dehydrogenation as the mechanism behind the superior electrochemical performance of the WO3 catalyst compared to W and NiO. Overall, the results are interesting, offering a new pathway for NOx upcycling. I recommend this manuscript for publication in Nat. Commun. with minor revisions and the following points should be addressed.
1. The authors should provide additional discussion regarding their choice of WO3 catalyst for synthesizing N2H4.
2. Is it possible DPK take part in reaction on the catalyst besides the formation of BPA?
3. In Figure S8, the authors demonstrated the isolation of N2H4 salts with similar crystal phases to commercial standard samples. While interesting, providing detailed yield rates of the isolated products and including experimental details on product synthesis in the Method section would enhance clarity.
4. In Figure 4g, the authors should further compare the electrostatic potentials of DMK-I, MPK-I, and DPK-I with free NH3 to elucidate the role of organic groups.
5. In Figure 5e, the authors compare the electrochemical performance in CH3CN and CH2Cl2, attributing the superior properties of acetonitrile solutions to hydrogen bonding. However, since the coherent properties of CH3CN and CH2Cl2 differ significantly, the authors should provide further discussion on the different electrochemical performances observed using CH3CN and CH2Cl2.
6. WO3 catalyst with W-O structure exhibited high performance for N-N coupling mediated by lattice-oxygen. Tunning the coordination structure of active sites is thus meaningful for breaking the limit of poor selectivity for the electrosynthesis of N2H4, which was demonstrated by the pioneer work has been reported in other electrocatalytic reactions I would like to suggest that some references should be discussed the introduction and discussion sections.

Reviewer #3 (Remarks to the Author):

Recommendation: publish after major revision

The authors demonstrated an interesting strategy to synthesise N2H4 through C-N coupling between NH3 and the ketone mediator and the N-N coupling of the imine. Convincing experiments were designed to prove the key roles of the WO3 catalyst, the acetonitrile solvent and the DPK mediator. This work provides a new electrosynthesis strategy and demonstrates how reaction selectivity towards N-N coupling can be controlled by tuning the reaction parameters I can support the publication in Nat Commun if the following points can be addressed.

1. I don’t think NOx reduction is really relevant to this study. The electrochemical conversion of NOx to NH3 is a useful reaction but it is unrelated to the reaction is this work. The whole point of NOx reduction

is to generate NH_3, and NH_3 is the actual starting material for the synthesis of N_2H_4. I would recommend the authors remove the part of NOx reduction and simply the procedures by just starting from NH_3, which is a common starting material for organonitrogen synthesis.

2. The potential vs Ag^+/Ag reference electrode is quite high. What is the overall cell voltage?

3. The control experiments for NiO, WO_3 and W catalysts are quite interesting. The authors should provide more in-depth investigations to reveal the roles of metal and oxygen, such as testing other metal oxide or metal hydroxide, and/or DFT calculations for the surface processes for NiO, WO_3 and W.

4. Figure 3f is quite confusing. What does it mean by 'ratio of conversion'? The three catalysts seem to all have 100% at initial condition, whereas in Figure 3d they have quite different conversion percentages. I guess the authors mean a normalised conversion? The authors should clarify it.

5. The discussions about the computation results in Figure 4c-f are not very convincing. The rate determining step should be from (1) to (2), where DMK has the smallest energy increase. The energy change from (2) to (3) is less important.

6. Following 5, the best way to confirm whether DPK-I is more stable than DMK-I and MPK-I would be measuring the relative amounts of imine vs ketone by NMR, when the three ketones are mixed with NH_3 in a solvent that can stablise imine (e.g. CH_2Cl_2).

7. The DFT calculations in Figure 5f do not support the authors' hypothesis that CH_3CN activates the N-H bond. The dehydrogenation step from R_2CNH^* to R_2CN^* becomes more endothermic in the presence of CH_3CN. It's also quite surprising to see the RDS is the desorption of the final product. Under what electrochemical potential was the calculations were performed? How many CH_3CN molecules were included in the model? And was the group without CH_3CN calculated in vacuum?

8. The author should also cite some recent reports on the electrochemical C-N coupling between ketone and inorganic nitrogen species, such as ACS Catal. 2024, 14, 3287–3297; Nanoscale, 2024, 16, 2805-2819; Nat. Commun. 2023, 14 (1), 3057. DOI: 10.1038/s41467-023-38888-6; Angew. Chem. Int. Ed. 2023, e202305491. DOI: 10.1002/anie.202305491.

Reviewer #4 (Remarks to the Author):

In this work, the authors propose a novel concept of a process for upgrading nitrate (NOx compounds in general) to hydrazine, following a three-step process including: i) an initial electrochemical reduction of nitrates to ammonia; ii) a ketone-mediated N-N coupling step by electrochemical oxidation of ammonia; iii) a hydrolysis step to convert the chemical N-N intermediate to hydrazine. The approach is sound, considering the intrinsic high selectivity values demonstrated for the individual steps, making the overall process appealing. Moreover, the study provides valuable insights into the electrochemical pathways for N_2H_4 production.

One important point about the work is that the title might be misleading as the approach does not follow a direct electrochemical step to reduce nitrate to hydrazine. In fact, the first step is a complementary aspect that might add value to the concept, but in general the source of NH3 does not condition the main idea of the work, which is the electrocatalytic N-N coupling of NH3 mediated by diphenyl ketone. Therefore, the authors should reconsider modifying the title to reflect the scope, mentioning that the source of NH3 can potentially be obtained from methods other than electrocatalysis.

- Check figure S1. The scheme shows that you are using Air for dragging NH3. However, the main manuscript and the legends of Figure S1 indicate that argon is the gas used for the purpose.
- Check lines 98-101, as figure S3 is the UV-vis NH3 calibration curve.
- With respect to the tests presented in figure 2, please indicate how long was the test at each applied potential.
- With respect to the five consecutive reutilization tests, please indicate the voltage at which the five cycles were performed.
- What is involved in the 88.7% Faradaic Efficiency? Only the conversion of NH3 to N2H4 or the FE of the whole system?
- Is it possible to ensure that all Nitrogen present in the N2H4 comes from NH3, and not from CH3CN during oxidation?
- From the last part of the text, the nature of the intermediate designated as DPK-I is clear. However, it is first mentioned in the description of the in-situ ATR-FTIR measurement. It would be helpful to have a definition earlier in the text.
- In line with the previous comment, the paragraph related to the in-situ ATR-FTIR mentions the formation and consumption of DPK-I and correlates it with reverse peaks. However, that contradicts the previous comment about the DPK-I signal intensification during electrolysis. Please elaborate more or indicate where these trends are observed, as no transient evolution is included.
- With respect to lines 183-187, the negligible direct electrocatalytic NOx reduction to N2H4 only proves the superior feasibility of the BPA-mediated N-N coupling from NH3, but certainly it doesn't state any specific requirement for NH3 generation route.
- In relation to the Raman analysis: although the intercalation of protons is plausible mechanism, Raman spectra of proton intercalated WO3 (HxWO3) in literature still show W-O related band. In this case, the progressive decrease of both O-W-O and W-O signals, mostly suggest a reduction of the surface. Related to this, the characterization of WO3 after electrolysis does not show significant variation. At which voltage was the electrolysis of this sample carried out? How does it correlate with the results of in-situ Raman?
- Please correct the title of figure S27, as it corresponds to the in-situ Raman measurement with NiO.
- Please explain better how the availability of H2O correlates with the low activity of NiO.

Reviewer #5 (Remarks to the Author):

I co-reviewed this manuscript with one of the reviewers who provided the listed reports. This is part of the Nature Communications initiative to facilitate training in peer review and to provide appropriate recognition for Early Career Researchers who co-review manuscripts

Responses to the comments of the reviewers

Reviewer 1

Han *et al.* demonstrated an innovative approach for upgrading NO_x wastes to valuable N_2H_4 (salts) chemicals through the integration of NO_x electroreduction to NH_3 and NH_3 oxidation to N_2H_4, employing a ketone mediator to moderate the N-N coupling process. They proposed lattice-oxygen-mediated dehydrogenation as the mechanism behind the superior electrochemical performance of the WO_3 catalyst compared to W and NiO. Overall, the results are interesting, offering a new pathway for NO_x upcycling. I recommend this manuscript for publication in ***Nat. Commun.*** with minor revisions and the following points should be addressed.

Response: We thank the reviewer very much for the comment, and we have carefully revised the manuscript based on the comments.

1. The authors should provide additional discussion regarding their choice of WO_3 catalyst for synthesizing N_2H_4.

Response: We thank the reviewer again for the comment. According to the comment, we would like to discuss the choice of WO_3 catalyst. WO_3 offers several advantages as an electrocatalyst, including a high density of active sites, moderate absorption for intermediates, good stability, and cost-effectiveness. These properties make it particularly advantageous for facilitating various electrochemical reactions. Additionally, we have performed the electrosynthesis of N_2H_4 using other catalysts, such as Pt/C, Fe_2O_3, CoO, and NiO. Among these catalysts, WO_3 demonstrated the best performance.

In the revised manuscript, we have discussed them by "Various catalysts commonly employed in electrocatalytic oxidation reactions, such as Pt/C, Ru/C, Pd/C, MnO_2, Fe_2O_3, CoO, NiO, and CuO, were screened. Noble metal-based catalysts exhibited poor catalytic performance for the oxidation of NH_3 to BPA, with Ru/C showing no catalytic activity. In contrast, transition metal-based catalysts (MnO_2, Fe_2O_3, CoO, NiO, CuO) can catalyze the reaction, albeit with inferior performance compared to WO_3. WO_3 exhibited the highest conversion of NO_x-derived NH_3 to BPA after electrolysis, as illustrated in Figure S4. As a result, WO_3 was identified as the optimal catalyst for N_2H_4 synthesis because of its numerous active sites and suitable binding affinity for intermediates." Please see them in Page 4 in the revised manuscript.

2. Is it possible DPK take part in reaction on the catalyst besides the formation of BPA?

Response: We thank the reviewer again for the comment. According to the GC-MS analysis of the electrolyte after electrolysis (Figure S5a), only BPA were detected as organic products. Consequently, the selectivity of the DKP-to-BPA conversion exceeds 99.9% under all applied potentials (Figure 2a), with no detectable by-products. Additionally, as shown in Figure S13, we demonstrated that DPK is highly inert in the absence of NH_3.

In the revised manuscript, we have discussed them by "The molecular weight of 360.1 determined by gas chromatography-mass spectrometry (GC-MS) showed that the product has the molecular formula of $C_{26}H_{20}N_2$ (Figure S5). In addition, the selectivity of DPK-mediated N-N coupling was as high as >99.9%, since no detectable by-product was observed in GC-MS." and "Furthermore, the findings from the linear sweep voltammetry (LSV) investigation in Figure S13 suggested the sluggish nature of the DPK reaction in the absence of NH_3, further supporting the preference for N-N coupling based on DPK-I intermediates." Please see them in Page 5 and Page 7 in the revised manuscript.

3. In Figure S8, the authors demonstrated the isolation of N_2H_4 salts with similar crystal phases to commercial standard samples While interesting, providing detailed yield rates of the isolated products and including experimental details on product synthesis in the Method section would enhance clarity.

Response: We thank the reviewer again for the comment. According to the comment, we have supplemented the experimental details of recrystallization of N_2H_4 salts by "The aqueous N_2H_4 solution was placed in a distillation flask, and the distillation apparatus was assembled. The solution was gradually heated to distill off the water, maintaining the temperature below the boiling point of hydrazine (114 °C) to prevent its loss. The concentrated hydrazine solution was then collected for further use. In a well-ventilated fume hood, concentrated HCl was added dropwise to the concentrated hydrazine solution with continuous stirring. The addition rate was carefully controlled to manage the exothermic reaction. HCl was added until the solution reaches a pH of < 1. The reaction mixture was cooled in an ice bath to promote the crystallization. The mixture is left in the ice bath for 2 hours to ensure complete crystallization. The hydrazine hydrochloride crystals were then isolated by vacuum filtration. The crystals were washed with a small volume of cold ethanol or acetone to remove impurities. Finally, the washed crystals were transferred to a drying oven set at 60 °C." in the supplementary information of the revised manuscript. In addition, we discussed the yield rates of the isolated products in the revised manuscript by "After recrystallization of N_2H_4-based products, we could obtain $N_2H_4 \cdot HCl$ and $(N_2H_4)_2 \cdot H_2SO_4$ products with a yield of >60%, which exhibited similar X-ray diffraction (XRD) patterns with commercial standard samples (Figure S8)." Please see them in Page 3 of the supplementary information and Page 5 in the revised manuscript.

4. In Figure 4g, the authors should further compare the electrostatic potentials of DMK-I, MPK-I, and DPK-I with free NH_3 to elucidate the role of organic groups.

Response: We thank the reviewer again for the comment. Compared with free NH_3, condensation into imine with ketone can significantly reduce the electrostatic potentials of N atom, which can further prove the importance of DPK for the synthesis of N_2H_4.

We further discussed this point by "Furthermore, the electrostatic potentials (φ_{max}) on the N atom side exhibited significant disparities for imines substituted with different groups: φ_{max}, DPK < φ_{max}, MPK < φ_{max}, DMK < φ_{max}, NH_3 (Figure 4c). This discrepancy could suggest that DPK-I has the capability to redistribute the charge density on the N atom of the imine group, thereby enhancing molecular stability." in the revised manuscript. Please see it in Page 11 in the revised manuscript.

5. In Figure 5e, the authors compare the electrochemical performance in CH_3CN and

CH_2Cl_2, attributing the superior properties of acetonitrile solutions to hydrogen bonding. However, since the coherent properties of CH_3CN and CH_2Cl_2 differ significantly, the authors should provide further discussion on the different electrochemical performances observed using CH_3CN and CH_2Cl_2.

Response: We thank the reviewer again for the comment. Generally, electrolyte solution includes supporting electrolytes, substrates, and solvents, forming a very complex system. Different solvents possess distinct physicochemical properties, which result in varying electrochemical behaviors in electrocatalytic reactions. In this work, we combined a variety of research methods, including ^1H NMR, ATR-FTIR, controlled experiments and DFT calculations demonstrated in Figure 5, to attribute the excellent performance of CH_3CN solvent to the existence of hydrogen bond between CH_3CN molecules and DPK-I intermediates.

In the revised manuscript, we have discussed them by "As a result, while we acknowledge the intrinsic complexity of solvent systems, the existence of hydrogen bond interaction between CH_3CN and DPK-I intermediates enhance the activation of N-H bonds, facilitating the N-N coupling of DPK-I intermediates, thus promoting BPA formation." Please see it in Page 12 in the revised manuscript.

6. WO_3 catalyst with W-O structure exhibited high performance for N-N coupling mediated by lattice-oxygen. Tunning the coordination structure of active sites is thus meaningful for breaking the limit of poor selectivity for the electrosynthesis of N_2H_4, which was demonstrated by the pioneer work has been reported in other electrocatalytic reactions. I would like to suggest that some references should be discussed the introduction and discussion sections.

Response: We thank the reviewer again for the comment. According to the comment, we have added some useful references, Ref. 37, Ref. 38, Ref. 39, and Ref. 40 into the revised manuscript (*Science*, **2024**, *384*, 670-676; *Angew. Chem. Int. Ed.*, **2024**, e202406947; *Nat. Commun.*, **2022**, *13*, 5382; *Nat. Commun.*, **2023**, *14*, 4209) and further discussed the importance of W-O structure in WO_3 catalyst in the revised manuscript by "The coordination structure of W-O active sites in the WO_3 catalyst is crucial for overcoming the limitations of poor selectivity in the electrosynthesis of N_2H_4. WO_3 can be rapidly and reversibly doped with hydrogen to form H_xWO_3 phase, significantly influencing reaction barriers and pathways, thereby enhancing catalytic performance.” Please see them in Page 9 in the revised manuscript.

Reviewer 3

Recommendation: publish after major revision

The authors demonstrated an interesting strategy to synthesize N_2H_4 through C-N coupling between NH_3 and the ketone mediator and the N-N coupling of the imine. Convincing experiments were designed to prove the key roles of the WO_3 catalyst, the acetonitrile solvent and the DPK mediator. This work provides a new electrosynthesis strategy and demonstrates how reaction selectivity towards N-N coupling can be controlled by tuning the reaction parameters I can support the publication in ***Nat. Commun.*** if the following points can be addressed.

Response: We thank the reviewer very much for the comment, which help and guide us to improve our work greatly. We have answered the questions from the reviewers and revised the manuscript on the basis of the comments.

1. I don't think NO_x reduction is really relevant to this study. The electrochemical conversion of NO_x to NH_3 is a useful reaction but it is unrelated to the reaction is this work. The whole point of NO_x reduction is to generate NH_3, and NH_3 is the actual starting material for the synthesis of N_2H_4. I would recommend the authors remove the part of NO_x reduction and simply the procedures by just starting from NH_3, which is a common starting material for organonitrogen synthesis.

Response: We thank the reviewer again for the comment. As the reviewer points out, the part of NH_3-to-N_2H_4 occupies a larger space, and NH_3 is the actual starting material for the synthesis of N_2H_4. However, considering the source of NH_3, such as using front-end NO_x as N source, in this process is novel and holistic, which is also innovative in the evolving field of NO_x upgrading. Traditional NO_x reduction methods typically yield only two thermodynamically stable products, N_2 and NH_3, with satisfactory selectivity. However, the production of value-added N_2H_4 from NO_x has not been previously reported. In our study, we demonstrated the synthesis of N_2H_4, thereby introducing a novel perspective to this field. We employed a cascading strategy to synthesize N_2H_4 from NO_x: first converting NO_x to NH_3, and subsequently converting NH_3 to N_2H_4 using DPK.

To avoid confusion, we have changed the title of our manuscript into "Upgrading of nitrate to hydrazine through cascading electrocatalytic ammonia production with controllable N-N coupling" in the revised version to better reflect this focus. Please see Page 1 in the revised manuscript.

2. The potential vs Ag/Ag$^+$ reference electrode is quite high. What is the overall cell voltage?

Response: We thank the reviewer again for the comment. The overall cell voltage at the optimal condition of 2.0 V vs Ag/Ag$^+$ was found to be 4.1 V. We acknowledge that the cell voltage during N_2H_4 synthesizing is high and it is a very challenging project to reduce the overall potential for minimize energy input.

In the revised manuscript, we have discussed this point by "At 2.0 V, NH_3 achieved the conversion rate to BPA as high as 98.5% and the overall cell voltage was found to be 4.1 V." Please see this in Page 6.

3. The control experiments for NiO, WO_3 and W catalysts are quite interesting. The authors should provide more in-depth investigations to reveal the roles of metal and oxygen, such as testing other metal oxide or metal hydroxide, and/or DFT calculations for the surface processes for NiO, WO_3 and W.

Response: We thank the reviewer again for the comment. According to the comment, we have further expanded the scope of our catalyst screening, and the conclusion remain unchanged. As shown in Figure 3 and Figure S4 of the revised manuscript, we have tested the oxidation of NH_3 to BPA with DPK using a wider range of electrocatalysts besides optimal WO_3, including Pt/C, Ru/C, Pd/C, MnO_2, Fe_2O_3, CoO, NiO, and CuO. Generally, the noble metals-based catalysts exhibited poor catalytic performance. The transition metal-based catalysts (MnO_2, Fe_2O_3, CoO, NiO, and CuO) can catalyze the reaction, but their performance is inferior to that of the optimal WO_3 catalyst.

Generally, Ni-based catalysts show excellent performance in the electrocatalytic oxidation of aqueous solutions (such as alcohols, aldehydes, and other organic molecules). This is because NiO reacts with H_2O to form NiOOH active sites, which have a high oxidation state of Ni, thereby promoting the oxidation of organic molecules. However, in acetonitrile solvent, the absence of water molecules prevents the formation of NiOOH, inhibiting the activity of Ni-based catalysts. In contrast, the WO_3 catalyst can promote the N-H bond dehydrogenation process in acetonitrile through the mediation of lattice oxygen (as described in Figure 3 of our manuscript). Thus, the WO_3 catalyst outperforms the Ni catalyst due to this lattice oxygen-mediated dehydrogenation mechanism.

In the revised manuscript, we have discussed them by "Various catalysts commonly employed in electrocatalytic oxidation reactions, such as Pt/C, Ru/C, Pd/C, MnO_2, Fe_2O_3, CoO, NiO, and CuO, were screened. Noble metal-based catalysts exhibited poor catalytic performance for the oxidation of NH_3 to BPA, with Ru/C showing no catalytic activity. In contrast, transition metal-based catalysts (MnO_2, Fe_2O_3, CoO, NiO, CuO) can catalyze the reaction, albeit with inferior performance compared to WO_3. WO_3 exhibited the highest conversion of NO_x-derived NH_3 to BPA after electrolysis, as illustrated in Figure S4." Please see Page 5.

4. Figure 3f is quite confusing. What does it mean by 'ratio of conversion'? The three catalysts seem to all have 100% at initial condition, whereas in Figure 3d they have quite different conversion percentages. I guess the authors mean a normalized conversion? The authors should clarify it.

Response: We thank the reviewer again for the comment. The normalized conversion was used when discussing the results shown in Figure 3f. In the revised manuscript, we have corrected the figure and please see it in Page 3 in the revised manuscript.

In the revised manuscript, we have discussed it by "As illustrated in Figure 3f, after Li^+ poisoning treatment, NiO and WO_3 catalysts experienced a substantial decrease in activity attributable to the strong coordination between Li^+ and lattice oxygen in NiO and WO_3 (Figure 3g)." Please see Page 10.

5. The discussions about the computation results in Figure 4c-f are not very

convincing. The rate determining step should be from (1) to (2), where DMK has the smallest energy increase. The energy change from (2) to (3) is less important.

Response: We thank the reviewer again for the comment. According to the comment, we reconsidered the influence of the transition state structure on the reaction steps and recalculated the energy of the relevant steps. Our revised calculations support the hypothesis that DPK is the most favorable for the formation of imines.

In the revised manuscript, we have discussed them by "To investigate the influence of ketone mediator molecules with varying electronic and steric properties (Figure 4b and Figure S28), we examined the energy changes involved in the condensation of three ketone with NH_3, such as dimethyl ketone (DMK), methyl phenyl ketone (MPK) and DPK. This led to the formation of imines, namely dimethyl ketone imine (DMK-I), methyl phenyl ketone imine (MPK-I), and DPK-I, following the removal of water molecules through the corresponding intermediates. The reaction transition state energy barriers from (1) to (2) for the ketones of DMK, MPK, and DPK were approximately the same, being 39.6, 39.1, and 39.4 kcal mol^{-1}, respectively. However, for the reaction process from (2) to (3), the transition state energy barriers decreased gradually to 52.0, 48.2, and 44.4 kcal mol^{-1}, respectively, indicating that the activity of the DMK-I, MPK-I, and DPK-I intermediates progressively increased. Hence, DPK exhibited a higher capacity for generating DPK-I due to the boosted dehydration process, which could serve as the mediator for single N-N coupling." Please see Page 11 of the revised manuscript.

6. Following 5, the best way to confirm whether DPK-I is more stable than DMK-I and MPK-I would be measuring the relative amounts of imine vs ketone by NMR, when the three ketones are mixed with NH_3 in a solvent that can stabiles imine (e.g. CH_2Cl_2).

Response: We thank the reviewer again for the comment. According to the comment, we also investigated the stability of the imine species derived from DPK-I, DMK-I, and MPK-I, and GC-MS analysis was used due to its lower detection limit. We mixed each ketone with NH_3 in CH_2Cl_2 and allowed the reaction to proceed overnight before subjecting the mixture to GC-MS. Our results indicated that no distinct imine species were observed for DMK and MPK. In contrast, for DPK, approximately 30% conversion to DPK-I species was detected. This suggested that the stability of DPK-I is significantly higher than that of DMK-I and MPK-I.

In the revised manuscript, we have discussed them by "The superior stability of DPK-I compared to DMK-I and MPK-I was further confirmed by GC-MS analysis (Figure S29). This analysis revealed that only DPK-I was detectable after mixing the corresponding ketone and NH_3." Please see Page 11 in the revised manuscript.

7. The DFT calculations in Figure 5f do not support the authors' hypothesis that CH_3CN activates the N-H bond. The dehydrogenation step from R_2CNH^* to R_2CN^* becomes more endothermic in the presence of CH_3CN. It's also quite surprising to see the RDS is the desorption of the final product. Under what electrochemical potential was the calculations were performed? How many CH_3CN molecules were included in the model? And was the group without CH_3CN calculated in vacuum?

Response: We thank the reviewer again for the comment. According to the comment, we have supplemented the electrochemical potential role in the simulation and discussed the calculation process in more detailed way in the revised manuscript, which can be found in the following.

1) Upon reevaluation, we investigated the catalytic process mediated by CH_3CN by applying a bias voltage range of 0.5-2.5 V. This adjustment resulted in changes of the free energy of reaction intermediates that support our initial hypothesis. Notably, the introduction of CH_3CN lowered the energy barrier for the dehydrogenation step and facilitated the overall reaction pathway. For example, when a bias voltage of 2.0 V was applied, the energy required for R_2CNH^* dehydrogenation to R_2CN^* decreased by 0.59 eV and the free energy for N-N coupling was reduced by 0.65 eV with CH_3CN was present. Furthermore, we acknowledge that the endothermic desorption of BPA product, which is a common phenomenon in electrocatalysis (*Nat. Commun.* **2023**, *14*, 3634; *Nat. Commun.* **2023**, 14, 8036; *Proc Natl Acad Sci*

USA **2023**, *120*, e2311149120; *Proc Natl Acad Sci USA* **2023**, *120*, e2312550120; *Adv. Mater.* **2023**, *36*, 2309470).

2) In our model, a single CH_3CN molecule was placed on the surface, and all simulations were conducted under vacuum conditions. These calculations have underscored the role of catalyst composition and structure in the observed effects, which agree with the experimental findings with theoretical calculations used to support and explain these results. Considering solvation effects, we further modified our catalyst models by incorporating one CH_3CN molecule on the surface. However, due to current computational limitations, it remains challenging to incorporate a larger number of CH_3CN molecules to simulate a continuous hydrogen bond network and compute reaction pathways within such a network.

We agree with the referee that exploring solvent effects on reactions is crucial for computational simulations that closely mimic real systems, but this remains a significant computational challenge requiring advancements in methodology and capabilities. Fortunately, these challenges do not affect the conclusions drawn in our paper regarding the superior electrochemical performance of WO_3 in CH_3CN solvent, as these conclusions were based on comparisons among different catalysts and electrolytes.

In the revised manuscript, we have discussed them by "Density Functional Theory (DFT) analysis shown in Figure 5f and Figure S30 revealed that in the presence of CH_3CN molecules, the energy required for R_2CNH^* dehydrogenation to R_2CN^* decreased by 0.59 eV compared to the absence of CH_3CN molecules, and the Gibbs free energy for the single N-N coupling step was reduced by 0.65 eV in the presence of CH_3CN. Furthermore, the energy barrier along the reaction path with CH_3CN was generally smoother than without CH_3CN. Hence, DFT calculations could elucidate the enhanced performance of DPK-I to BPA with the assistance of CH_3CN solvent." Please see Page 13 in the revised manuscript.

8. The author should also cite some recent reports on the electrochemical C-N coupling between ketone and inorganic nitrogen species, such as *ACS Catal.* **2024**,

14, 3287-3297; *Nanoscale*, **2024**, *16*, 2805-2819; *Nat. Commun.* **2023**, *14*, 3057; *Angew. Chem. Int. Ed.* **2023**, *62*, e202305491.

Response: We thank the reviewer again for the comment. The recommended references are very useful and we have added them as Ref. 9, Ref. 10, Ref. 12, and Ref. 13, respectively, in the revised manuscript. We have discussed these references by "The excessive emission of nitrogen oxides (NO_x) poses environmental and human health concerns, but they also serve as renewable nitrogen sources for the synthesis of value-added chemicals driven by clean energy." and "NO_x electroreduction is a multi-electron transfer process involving various intermediates, most of which are unstable and fleeting." in the revised manuscript. Please see them in Page 2 in the revised manuscript.

Reviewer 4

In this work, the authors propose a novel concept of a process for upgrading nitrate (NO_x compounds in general) to hydrazine, following a three-step process including: i) an initial electrochemical reduction of nitrates to ammonia; ii) a ketone-mediated N-N coupling step by electrochemical oxidation of ammonia; iii) a hydrolysis step to convert the chemical N-N intermediate to hydrazine. The approach is sound, considering the intrinsic high selectivity values demonstrated for the individual steps, making the overall process appealing. Moreover, the study provides valuable insights into the electrochemical pathways for N_2H_4 production.

Response: We appreciate the valuable feedback from the reviewer and have thoroughly revised the manuscript in accordance with the comments.

One important point about the work is that the title might be misleading as the approach does not follow a direct electrochemical step to reduce nitrate to hydrazine. In fact, the first step is a complementary aspect that might add value to the concept, but in general the source of NH_3 does not condition the main idea of the work, which is the electrocatalytic N-N coupling of NH_3 mediated by diphenyl ketone. Therefore, the authors should reconsider modifying the title to reflect the scope, mentioning that the source of NH_3 can potentially be obtained from methods other than electrocatalysis.

Response: We thank the reviewer again for the comment. As the reviewer points out, the part of NH_3-to-N_2H_4 occupies a larger space, and NH_3 is the actual starting material for the synthesis of N_2H_4. However, considering the source of NH_3, such as using front-end NO_x as N source, in this process is novel and holistic, which is also innovative in the evolving field of NO_x upgrading. Traditional NO_x reduction methods typically yield only two thermodynamically stable products, N_2 and NH_3, with satisfactory selectivity. However, the production of value-added N_2H_4 from NO_x has not been previously reported. In our study, we demonstrated the synthesis of N_2H_4, thereby introducing a novel perspective to this field. We employed a cascading strategy to synthesize N_2H_4 from NO_x: first converting NO_x to NH_3, and subsequently converting NH_3 to N_2H_4 using DPK.

To avoid confusion, we have changed the title of our manuscript into "Upgrading of nitrate to hydrazine through cascading electrocatalytic ammonia production with controllable N-N coupling" in the revised version to better reflect this focus. Please see Page 1 in the revised manuscript.

1. Check figure S1. The scheme shows that you are using air for dragging NH_3. However, the main manuscript and the legends of Figure S1 indicate that argon is the gas used for the purpose.

Response: We thank the reviewer again for the comment. We apologize for the error in Figure S1. In this work, to avoid introducing other impurities to affect the reaction, we utilized Ar as the load gas to transfer NH_3 form the aqueous system to the organic solution. We have corrected Figure S1 in the revised manuscript. Please see Page 6 in the supplementary information.

2. Check lines 98-101, as figure S3 is the UV-vis NH_3 calibration curve.

Response: We thank the reviewer again for the comment. According to the comment, we have re-described this point by "The electrocatalytic reduction of NO_x to NH_3, utilizing aqueous NO_3^- as an example, was performed using an H-type cell, employing commercial oxide-derived copper (OD Cu) as catalyst (Figure S2). The NH_3 product obtained from electroreduction was detected using the well-established salicylate method as is demonstrated in Figure S3." in the revised manuscript to avoid misunderstanding. Please see it in Page 4 in the revised manuscript.

3. With respect to the tests presented in figure 2, please indicate how long was the test at each applied potential.

Response: We thank the reviewer again for the comment. According to the comment, we have discussed the electrolysis time in the revised manuscript by "The electrocatalytic N-N coupling performance using NO_x-derived NH_3 and DPK in CH_3CN solvent was evaluated through electrolysis conducted over WO_3 catalyst within a voltage range of 1.2 V to 2.2 V vs Ag/Ag^+ for 10 h (Figure S10)." Please see them in

Page 6 in the revised manuscript.

4. With respect to the five consecutive reutilization tests, please indicate the voltage at which the five cycles were performed.

Response: We thank the reviewer again for the comment. The reutilization tests were conducted at optimal 2.0 V in our work. We have discussed this point by "After being employed five times consecutively at optimal 2.0 V, the WO_3 catalyst maintained a stable current during electrolysis, achieving a NH_3 to BPA conversion rate of 99.2% and a BPA FE of 94.7% (Figure S11)." in the revised manuscript. In addition, we have presented the applied potential in Figure S11 in the supplementary information. Please see them in Page 6 in the revised manuscript and Page 16 in the supplementary information.

5. What is involved in the 88.7% Faradaic Efficiency? Only the conversion of NH_3 to N_2H_4 or the FE of the whole system?

Response: We thank the reviewer again for the comment. In this work, we demonstrated a cascade strategy to upgrade NO_3^- to N_2H_4 with an excellent overall selectivity of 88.7%. It should be noted that this 88.7% is not the FE of any single electrochemical reaction, but rather the conversion rate of NO_3^- to N_2H_4. We conversed 88.7% of the initial NO_3^- substrate to N_2H_4 product through the demonstrated strategy.

In the revised manuscript, we have emphasized it by "As a result, this tandem process exhibits remarkable efficiency, and the overall selectivity of NO_x-to-N_2H_4 was 88.7%." Please see Page 5.

6. Is it possible to ensure that all nitrogen present in the N_2H_4 comes from NH_3, and not from CH_3CN during oxidation?

Response: We thank the reviewer again for the comment. According to the comment, we have supplemented the ^{15}N isotopic labeling experiments in the revised manuscript. The MS analysis revealed the presence of a signal at *m*/*z* of 362.1, which could be attributed to the ^{15}N-labeled BPA. This finding could further support the conclusion that the nitrogen source for both BPA and N_2H_4 was derived from the nitrate substrates, ruling out the influence of other contaminants under the experimental conditions.

In the revised manuscript, we have shown the result as Figure S5 and discussed it by "By employing $K^{15}NO_3$ as the reactant, we detected a molecular ion peak of the product at 362.1 (Figure S5e), precisely matching the calculated molecular weight of $C_{26}H_{20}{}^{15}N_2$. This finding confirmed that the nitrogen source in BPA was derived from nitrate." Please see Page 5 in the revised manuscript.

7. From the last part of the text, the nature of the intermediate designated as DPK-I is clear. However, it is first mentioned in the description of the in-situ ATR-FTIR measurement. It would be helpful to have a definition earlier in the text.

Response: We thank the reviewer again for the comment. According to the comment, we have added the corresponding description in the revised manuscript: "The evolution of intermediates during BPA formation was further studied utilizing *in situ* ATR-FTIR spectroscopy. The peaks at 1674 cm^{-1} (Figure 2c), 1597 cm^{-1} (Figure 2d), 1570 cm^{-1} (Figure 2d), and 1450 cm^{-1} (Figure 2e) corresponded to the H_2O produced after C-N condensation between NH_3 and DPK, the active C-N bonds in Ph_2CN^* intermediates, the DPK mediator consumed during the reaction, and the diphenyl ketone imine (DPK-I) intermediates respectively." Please see them in Page 6 in the revised manuscript.

8. In line with the previous comment, the paragraph related to the in-situ ATR-FTIR mentions the formation and consumption of DPK-I and correlates it with reverse peaks. However, that contradicts the previous comment about the DPK-I signal intensification during electrolysis. Please elaborate more or indicate where these trends are observed, as no transient evolution is included.

Response: We thank the reviewer again for the comment. It was observed that the intensity of signals of H_2O and C=N increased during electrolysis, but that of C=O and N-H were decreased. The signals indicated the concentration of species containing C=N (including Ph_2CN^* and BPA) was increased. In contrast, the DPK and DPK-I signals corresponding to C=O and N-H, respectively, were gradually diminished. In addition, the C=N structure exists both before and after the N-N coupling, resulting in the gradual enhancement of the C=N signal.

In the revised manuscript, we have discussed them by “Moreover, the observed signals of H_2O and Ph_2CN*/DPK-I (C=N) was intensified during electrolysis, indicating an increased concentration of these intermediates in the solution, while the signal corresponding to DPK (C=O) and DPK-I (N-H) demonstrated reverse peaks, confirming its consumption. Thereinto, as DPK-I underwent N-N coupling to form BPA, the N-H signal gradually diminished. The C=N structure co-existing in both DPK-I and BPA contributed to a gradual rise in the C=N signal.” Please see them in Page 6 in the revised manuscript.

9. With respect to lines 183-187, the negligible direct electrocatalytic NO_x reduction to N_2H_4 only proves the superior feasibility of the BPA-mediated N-N coupling from NH_3, but certainly it doesn't state any specific requirement for NH_3 generation route.

Response: We thank the reviewer again for the comment. In fact, there is no difference in N_2H_4 generation between NO_x-derived NH_3 and direct NH_3 feeding. Our demonstration based on NO_x was to show the pathway to converting renewable NO_x resources into value-added N_2H_4. To avoid misunderstanding, we have discussed this point by “This reiterated the necessity of BPA-mediated N-N coupling processes based on NH_3 as a direct nitrogen source during N_2H_4 generation.” in the revised manuscript. Please see it in Page 7 of the revised manuscript.

10. In relation to the Raman analysis: although the intercalation of protons is plausible mechanism, Raman spectra of proton intercalated WO_3 (H_xWO_3) in literature still show W-O related band. In this case, the progressive decrease of both O-W-O and W-O signals, mostly suggest a reduction of the surface. Related to this, the characterization of WO_3 after electrolysis does not show significant variation. At which voltage was the electrolysis of this sample carried out? How does it correlate with the results of in-situ Raman?

Response: We thank the reviewer again for the comment. The interactions between protons and WO_3 catalysts, leading to the formation of active H_xWO_3 species, have been extensively documented in various electrocatalytic studies (*Nat. Commun.* **2022**, *13*, 5382; *Nat. Commun.* **2023**, *14*, 4209; *Nano Energy* **2020**, *71*, 104653). These investigations consistently showed that as the applied potential increases, the intensity of the W-O signal gradually diminishes until it becomes undetectable. Thus, the Raman spectroscopy results presented in this manuscript supported the proposed mechanism involving lattice oxygen-mediated dehydrogenation processes to produce BPA products. Thereinto, the potential range used for in situ Raman spectroscopy closely matched that employed in electrochemical performance testing. Additionally, H_xWO_3, identified as an active species existing on the catalyst surface, could not induce bulk phase transitions in the WO_3 catalyst. Consequently, post-electrolysis tests confirm that the structure of the used WO_3 remained similar to that of the initial WO_3, which was consistent with findings reported in recent literature.

In the revised manuscript, we have discussed them by "H_xWO_3, recognized as an active species present on the catalyst surface, could not drive bulk phase transitions in the WO_3 catalyst. Therefore, post-electrolysis tests verify that the structure of the used WO_3 remained comparable to its initial state." Please see Page 9 in the revised manuscript.

11. Please correct the title of figure S27, as it corresponds to the in-situ Raman measurement with NiO.

Response: We thank the reviewer again for the comment. According to the comment, we have corrected the title of Figure S27 in the supplementary information of the revised manuscript. Please see Page 32 in the supplementary information.

12. Please explain better how the availability of H_2O correlates with the low activity of NiO.

Response: We thank the reviewer again for the comment. In the electrocatalytic oxidation reaction involving H_2O molecules, NiO catalyst typically reacts with H_2O to produce NiOOH active site, involving high oxidation state Ni species (*Chem* **2022**, *6*, 2974-2993). However, in CH_3CN solvents, there is no interaction between H_2O molecules and NiO sites to produce NiOOH, thereby limiting the activity of Ni-based catalyst.

In the revised manuscript, we have discussed them by "As a result, electrooxidation reaction on NiO was not favorable due to the limited availability of H_2O in CH_3CN solvents hindering the generation of active NiOOH site from NiO and H_2O." Please see them in Page 9 in the revised manuscript.

Reviewer 5

I co-reviewed this manuscript with one of the reviewers who provided the listed reports. This is part of the ***Nature Communications*** initiative to facilitate training in peer review and to provide appropriate recognition for Early Career Researchers who co-review manuscripts.

Response: We sincerely thank you for your valuable contribution to reviewing our manuscript. We appreciate your efforts and wish you all the best in your future career endeavors.

REVIEWERS' COMMENTS

Reviewer #1 (Remarks to the Author):

No more comments.

Reviewer #3 (Remarks to the Author):

The authors have addressed all my comments as well as other reviewers. The manuscript should be published in Nat Commun.

Reviewer #4 (Remarks to the Author):

As commented for the previous version, in this work the authors propose an innovative concept for hydrazine synthesis from ammonia and nitrates, based on a multi-step process. The focus is more specific towards the electrochemical oxidation of ammonia, although the study encompasses a wider perspective involving an initial reduction of nitrate into ammonia.
The values achieved and the concept itself are interesting, and the authors provide insights into mechanistic aspects related to the generation of N2H4, mostly to the effect of ketones and solvents.

For the present version, the authors have carefully considered the reviewers' comments, and have carried out either additional measurements or have provided responses to certain unclear points. Moreover, they have modified and revised the manuscript accordingly.

Therefore, I can recommend its publication in the present form.

Responses to the comments of the reviewers

Reviewer 1:

No more comments.

Response: We thank the reviewer very much for the positive comment.

Reviewer 3:

The authors have addressed all my comments as well as other reviewers. The manuscript should be published in Nat Commun.

Response: We thank the reviewer very much for the positive comment.

Reviewer 4:

As commented for the previous version, in this work the authors propose an innovative concept for hydrazine synthesis from ammonia and nitrates, based on a multi-step process. The focus is more specific towards the electrochemical oxidation of ammonia, although the study encompasses a wider perspective involving an initial reduction of nitrate into ammonia.

The values achieved and the concept itself are interesting, and the authors provide insights into mechanistic aspects related to the generation of N_2H_4, mostly to the effect of ketones and solvents.

For the present version, the authors have carefully considered the reviewers' comments, and have carried out either additional measurements or have provided responses to certain unclear points. Moreover, they have modified and revised the manuscript accordingly.

Therefore, I can recommend its publication in the present form.

Response: We thank the reviewer very much for the positive comment.