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Perspective

Progress and perspectives in the electroreduction of low-concentration nitrate for wastewater management

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SUMMARY

The electroreduction of nitrate has emerged as a promising global strategy for water purification in the face of harmful nitrate in wastewater. However, the usually low concentration of nitrate in wastewater poses a great challenge to this process, thus necessitating more in-depth studies to optimize its efficiency. This perspective article briefly explores the various electrochemical pathways of nitrate reduction, including the conversion of nitrate to ammonia, the conversion of nitrate to dinitrogen, and the C-N coupled reduction process. In addition, the feasibility of the electroreduction method is assessed from the concentration nitrate sources, reactor design, and promising energy sources, while also offering insights into prospective developments for further research.

INTRODUCTION

The proliferation of anthropogenic activities, such as the overuse of fertilizers in agriculture and the emission of pollutants from industry, have thrown the global nitrogen cycle off balance.[1,2] Nitrate-N (NO_3^-), as a widespread nitrogenous substance in water, poses numerous detrimental impacts on both aquatic ecosystems and human health, leading to issues such as eutrophication in aquatic environments and the disease such as methemoglobinemia.[3,4] The emphasis on human health and sustainable development has indeed led to the exploration and application of various conventional nitrate removal strategies.

Over the past decades, several approaches have been employed to address this human-induced nitrate pollution, each with its own set of advantages and limitations.[1,5] Physical removal methods such as ion exchange and reverse osmosis are very general methods for wastewater treatment.[6,7] Although these strategies are effective for removing the nitrate and can be tailored to target specific contaminants, they focus on the displacement rather than elimination. Therefore, this process would produce brine solutions, leading to the production of salty waste streams that need to be managed. As for biological-removal approaches, this method utilizes microorganisms to convert nitrate into nitrogen, which is then released into the atmosphere.[8] Biological denitrification can be a cost-effective and sustainable option, as it leverages natural processes and does not produce hazardous waste. However, given the life-giving nature of microorganisms, environmental conditions need to be carefully controlled to ensure the efficiency and stability of the microbial community. In contrast, the chemical reduction method is increasingly seen as a promising approach for converting nitrate pollutants into harmless and even valuable products using chemical reagents or catalysts. Various driving forces, including heat, light, and electricity, have been investigated to initiate and sustain the reduction reactions. Among them, the electrochemical reduction of nitrate offers a highly promising method due to its the utilization of environmentally friendly electrons as reducing agents, its operation under ambient conditions, and the elimination of the need for secondary treatment processes.[9]

Generally, the method of electric-driven nitrate reduction reaction (NO_3RR) would mainly lead to two main pathways, involving the reduction of nitrate to harmless dinitrogen or its conversion into ammonia, which carries additional value.[10,11] Furthermore, integrating nitrate removal from wastewater with carbon dioxide reduction (C-N coupling) to synthesize value-added organonitrogen compounds has demonstrated even greater commercial potential. For instance, urea, as previously reported, could achieve a market valuation of 75.0 billion USD, surpassing that of ammonia at 71.98 billion USD.[12,13]

At the early stage of the research on electrochemical nitrate reduction, the emphasis was predominantly on understanding the reaction mechanisms from the chemical standpoint, overlooking the real-world scenario of low nitrate concentrations in wastewater, as experiments were typically conducted at nitrate concentrations exceeding 0.1 M. However, especially after 2019, with more attention brought to the wastewater conversion, there has been a noticeable shift toward investigating the electroreduction of nitrate at lower concentrations, targeting its practical applicability. The trend of publication originating from the Web of Science database is shown in Figure 1. This article offers a comprehensive review of the latest advancements in the field of low-concentration nitrate electroreduction from three aspects, exploring various methodologies and assessing the practical and economic viability of this approach in wastewater treatment.

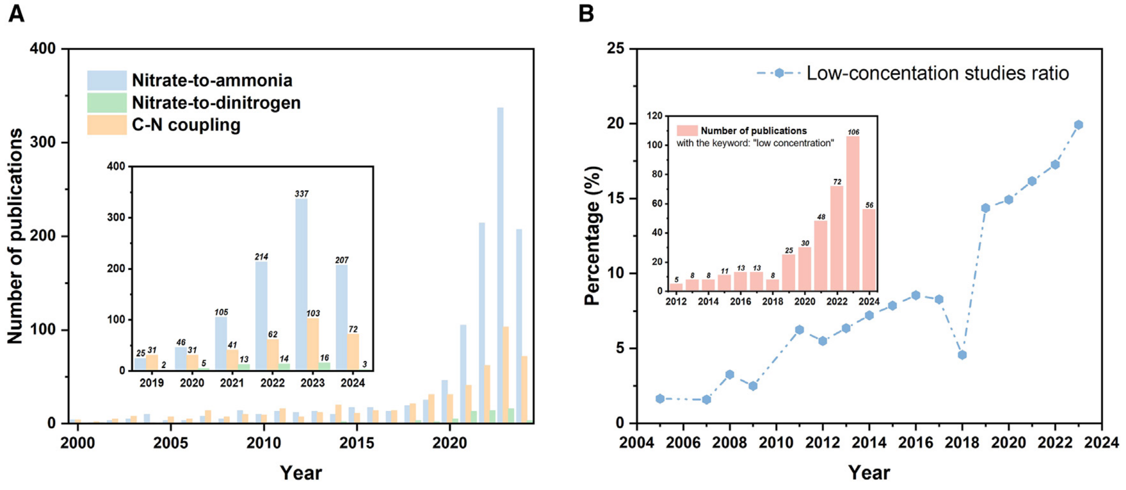

Figure 1. Publications development trend of nitrate reduction

(A) Publications of nitrate reduction from the three aspects since 2000.

(B) The ratio of publication numbers with keywords "electrochemical nitrate reduction at low concentration" to "electrochemical nitrate reduction" since 2005. The data are originated from the *Web of Science* database searched on June 25th, 2024.

The electrochemical strategy discussed herein emerges as a promising avenue for generating economic value and achieving the synergistic mitigation of nitrate pollution in wastewater, embodying the principle of "turning waste into wealth."

RESEARCH PROGRESS ON DIRECT NITRATE REDUCTION AT LOW CONCENTRATION

The promising prospect of nitrate reduction applied in wastewater management has attracted great concern recently. Considering the broad valence state range of N from +5 in NO_3^- to −3 in NH_3, the reduction of nitrate would lead to various possible products and complex reaction pathways (Figure 2).[14,15] The mechanism of this reduction reaction is highly dependent on the NO_3^- concentration and pH value of the electrolyte, which has been thoroughly discussed previously.[15,16] In general, nitrate reduction at relatively low concentrations can be categorized into two groups based on the main products: conversion of nitrate to ammonia and conversion of nitrate to nitrogen. The equations for the two reactions are listed as below[17]:

$$2NO_3^- + 12H^+ + 10e^- \rightarrow N_2 + 6H_2O \quad E^0 = 1.17 \text{ V vs. SHE}$$

$$NO_3^- + 9H^+ + 8e^- \rightarrow NH_3 + 3H_2O \quad E^0 = -0.12 \text{ V vs. SHE}$$

In the electrolyte with low nitrate concentration (<0.1 M), the efficiencies of NO_3RR for both the two end products are significantly constrained by the competitive hydrogen evolution reaction (HER), which would become severe under more acidic conditions with a lower energy barrier. The equation for HER is listed as below:

$$2H^+ + 2e^- \rightarrow H_2 \quad E^0 = 0.00 \text{ V vs. SHE}$$

With high surface coverage of hydrogen, the access of nitrate ions to the catalyst surface would be limited.[15] However, it is notable that protons also play a critical role in NO_3RR, modulating the activity and selectivity for N_2/NH_3 generation.[18] Wang et al. investigated the effect of various hydrogen species including hydrogen gas (H_2), hydrogen ion (H^+), and hydrogen atom (H^*). Their experimental results revealed that an increased presence of H^* tends to favor the formation of N_2. Conversely, a disparity between H^* and NO_3^- levels results in diminished selectivity for N_2, while enhancing the selectivity for NH_3 production. This observation aligns with the noted preference for ammonia synthesis at relatively high concentrations of nitrate.[19] Besides, the adsorption characteristics of N and O for each catalyst have a significant impact on product selectivity.[15,20] Drawing upon the theoretical analysis conducted by Liu et al., the formation of N_2 requires the robust adsorption of both O and N across all potential ranges, as observed with catalysts such as Fe and Co. Conversely, catalysts exhibiting moderate adsorption characteristics for O and N, such as Rh, tend to favor selectivity toward NH_3 production. Typically, the generation of NH_3 is facilitated at more negative potentials, while the production of N_2 is favored at more positive potentials.

The rapid advancement of *in situ* characterization techniques significantly enhances our understanding of the NO_3RR mechanism and informs catalyst design. Unlike traditional *ex situ* methods that provide only indirect insights, *in situ* techniques offer direct and precise information about active species and intermediates during the reaction. Techniques such as *in situ* spectroscopy (e.g., Raman, FTIR, and XPS) and *in situ* microscopy (e.g., scanning tunneling microscopy) enable researchers to observe real-time changes in catalyst surface composition and structure. This capability is crucial for elucidating the mechanisms of various ammonia production pathways and understanding the impact of different conditions on the reaction. By capturing the dynamic nature of the process, *in situ* techniques facilitate the optimization of electrocatalysts and reaction conditions, ultimately improving the efficiency and selectivity of ammonia production.[9,21,22]

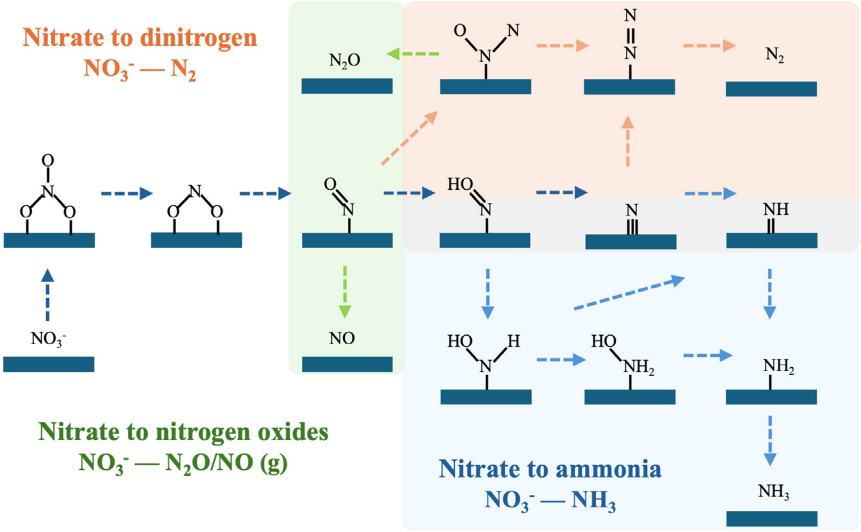

Figure 2. The schematic of the mechanism of electrochemical NO_3RR toward dinitrogen and ammonia

Despite the potential of the nitrate electroreduction to yield various products such as NH_3 and N_2, each pathway presents its unique application scenarios in the context of wastewater management.

The high-value added ammonia recovered from nitrate-contained wastewater offers an alternative to the traditional Haber-Bosch process, which requires high temperatures, and high pressures, and even results in the substantial consumption of fossil fuels. This nitrate-to-ammonia conversion has raised great interest of researchers and has been widely reported. In 2022, Chen et al. reported a Ru-dispersed Cu nanowire catalyst for the electroreduction of nitrate source at a typical industrial concentration level. This high NO_3RR activity enabled an over 99% nitrate-to-ammonia rate and realized a nitrate removal from 2000 ppm (equal to 33 mM NO_3^-) to less than 50 ppm, meeting the drinking-water safety standard set by the World Health Organization (WHO).[23] Similarly, our group designed a CuCo nanowires catalyst based on the tandem catalysis mechanism of NO_3RR and investigated its performance in a large-scale prototype (Figures 3A and 3B). Finally, the scaling-up reactor realized a gram-level ammonia yield rate of 1474.09 mg h^{-1} with Faraday efficiency of 91.26% from 2000 ppm nitrate electrolyte at 20.0 A.[24] However, the ammonia production performance could be greatly affected by the nitrate concentration in the electrolyte. Generally, at lower nitrate concentrations (e.g., 10 mM and 5 mM), the conversion efficiency decreases significantly, primarily due to the limited mass transfer of nitrate ions at the electrode surface and the occurrence of competing side reactions. Recently, there have been reports of the NO_3RR at ultra-low nitrate concentrations.[25–27] With this in mind, various strategies from developing highly efficient catalysts to modulating local nitrate concentrations have been investigated. Single atom-based catalysts have proven high efficiency for NO_3RR due to the unique electronic properties and highly dispersed active sites. In particular, the interaction between metal atoms (M) and nitrogen atoms (N) can result in the formation of an unsaturated coordination motif ($M–N_x$), which has implications for the binding energy of various reaction intermediates.[28–30] This interaction fosters a robust metal-support synergy, which in turn augments the catalytic activity of the metal sites. This enhancement is further supported by the influence of adjacent atoms within the substrate, which contribute to the overall reactivity. The single atom catalyst Cu-N_3C_1 SAC was synthesized and demonstrated an efficiency of approximately 95% in converting nitrate to ammonia, effectively reducing the nitrate concentration in wastewater from 100 ppm (equal to 1.6 mM NO_3^-) to 5 ppm at -0.64 V vs. RHE.[31] In addition, the superior nitrate reduction performance was proved through charge density differences. Compared to the NC and Cu(II)-N_4, Cu(I)-N_3C_1 shows electron depletion at the central Cu(I) while the charge density at the N_3C_1 site would decrease, leading to favorable charge transfer and stronger interaction between Cu(I) and N_3C_1 (Figures 3C–3E). Xiao et al. developed a core-shell structure $CoCuO_x@CuO_x$/CF, forming a built-in electric field at the interface which greatly improved the nitrate removal and ammonia production performance. Even at the ultra-low nitrate concentration of 1 mM, this catalyst realized the ammonia yield rate of $519.1\ \mu g\ h^{-1}\ cm^{-2}$ along with the Faraday efficiency of 99.83%.[32] Besides, modulating the ionic micro-environment at the electrode-electrolyte interface is another promising solution strategy for NO_3RR at ultra-low nitrate concentrations. Specifically, pulse electrolysis could offer intrinsic advantages by periodically altering the potentials that are inaccessible under conventional potentiostatic conditions. Huang et al. applied the pulsed potential approach, realizing the good NO_3RR performance of Faraday efficiency at 97.6% and yield rate of $2.7\ mmol^{-1}\ h^{-1}\ mg_{Ru}^{-1}$ at 10 mM.[33]

Despite numerous studies promoting the advancement of nitrate electroreduction to ammonia, there remain unresolved debates concerning the practicality of applying nitrate-to-ammonia conversion in wastewater treatment. Specifically, the requirement for subsequent processes to separate and convert dilute ammonium from mixed waste streams into usable forms of pure ammonia raises questions about the overall feasibility of nitrate-to-ammonia conversion. This issue highlights the significance of further research into the closed-loop NO_3RR pathway, encompassing both wastewater pretreatment and ammonia extraction.[9,35] Conversely, some scholars argue that reducing nitrate to environmentally harmless dinitrogen might represent a more feasible approach, particularly when dealing with low nitrate concentrations in wastewater.[18] As previously mentioned, enhancing the selectivity toward dinitrogen can be achieved by designing catalysts and modulating the intermediates and atomic hydrogen involved in the reaction process. There have been few electrocatalysts developed for nitrate-to-dinitrogen conversion in recent years, and the synergism between Cu and Pd has been reported effective for this reaction. In this

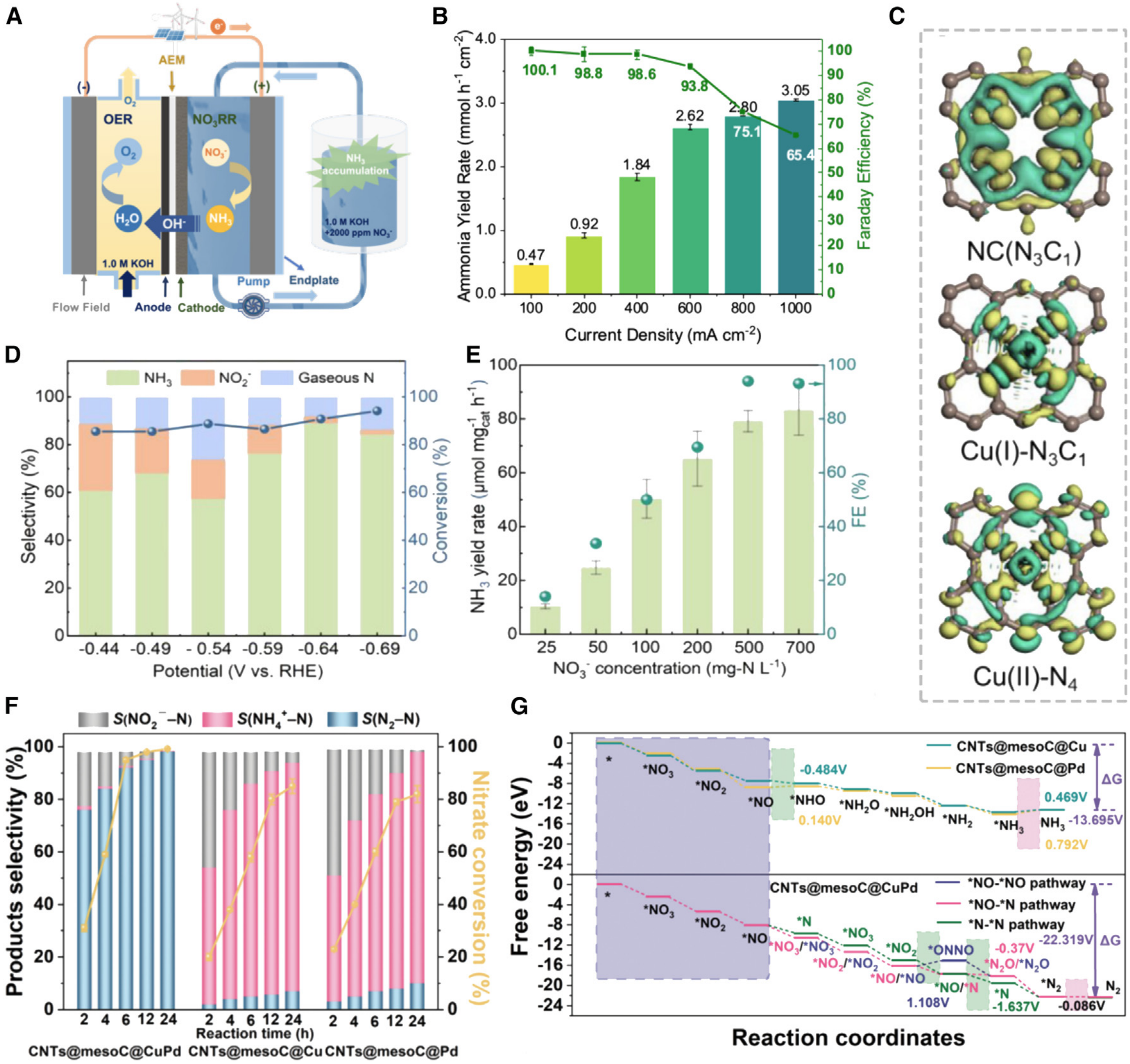

Figure 3. Reported NO_3RR performance

(A) The schematic illustration and the working principle for the flow reactor.

(B) FE and ammonia yield rate at high current densities (1.0 M KOH +2000 ppm NO_3^-). Copyright 2024, Wiley-VCH GmbH.[24]

(C) Charge density difference of NC, Cu(I)-N_3C_1, and Cu(II)-N_4.

(D) Nitrate conversion and nitrogen species product selectivity of different cathode potentials.

(E) Ammonia yield rate and FE under different initial concentrations. Copyright 2022, American Chemical Society.[31]

(F) The evolution of NO_3^--N conversion and products selectivity on different electrodes.

(G) The free energies of reaction pathways by theoretical calculation for different intermediates over the CNTs@mesoC@Cu, CNTs@mesoC@Pd, and CNTs@mesoC@CuPd. Copyright 2022, Wiley-VCH GmbH.[34]

synergistic relationship, Cu functions as a catalyst for the reduction of NO_3^- to NO_2^-, while Pd provides the active hydrogen species necessary for promoting the coupling of nitrogen atoms, a critical step in the overall reaction pathway to dinitrogen.[36] As a representative study, Xu et al. reported the *in situ* confinement of CuPd nanoparticles in a core-shell structure carbon nanotubes enveloped by mesoporous carbon (CNTs@mesoC@CuPd).[34] The synthesized CNTs@mesoC@CuPd demonstrated exceptional electrocatalytic capabilities, achieving nearly complete nitrate removal efficiency and dinitrogen selectivity. As shown in Figure 3F, during the initial reduction stage, the generation of NO_2^- and NH_4^+ was observed and eventually transformed into N_2 over time. The catalyst also exhibited the outstanding cycling stability of over 30 days with an initial low nitrate concentration of 100 mg L^{-1} (equivalent to 1.6 mM NO_3^-). The mechanism of nitrate-to-dinitrogen conversion was investigated through the free energies of reaction pathways by theoretical calculations (Figure 3G). In addition, it has been reported that the development of an open-framework cathode featuring electron-rich cobalt sites could exhibit exceptional performance in providing atomic hydrogen.[35] Xu et al. reported the synthesis of highly porous, Co PBA nanocrystals with tunable metal centers on graphene oxide

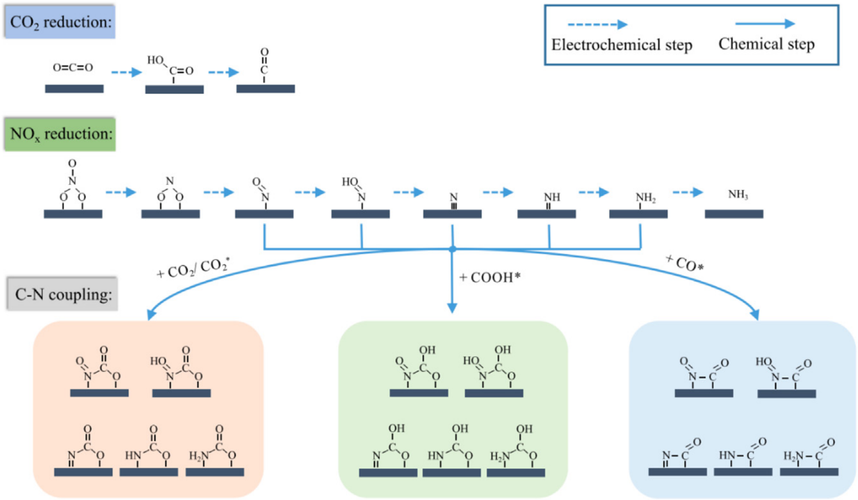

Figure 4. The schematic of the mechanism of electrochemical C-N coupling toward different end products

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sheets. Benefiting from enhanced mass transfer and the ready supply of atomic hydrogen, the electrode showcased exceptional performance in nitrate removal and N_2 selectivity at a nitrate concentration of 50 mg-N L^{-1} (equivalent to 3.6 mM NO_3^-). It achieved a nitrate removal efficiency of 100% and the N_2 Faraday efficiency of 97.89%, indicating its high efficacy in nitrate-to-dinitrogen processes. Additionally, a variety of novel materials have been identified as potential catalysts capable of attaining high nitrogen selectivity and nitrate removal rates, including Prussian blue analogs, MXenes, and metal-based single-atom catalysts, and so forth. However, despite their potential, the kinetics of the nitrate to dinitrogen conversion is still low, with high nitrate removal rates and nitrogen selectivity typically realized only after prolonged electrolysis exceeding 6 h.[37]

In summary, from a mechanistic standpoint, both nitrate reduction pathways—nitrate-to-ammonia and nitrate-to-dinitrogen—are theoretically viable, yet each presents distinct challenges when considered for practical wastewater treatment applications. Specifically, the conversion of nitrate to ammonia introduces complexities associated with the subsequent separation of ammonia, which poses a significant challenge. Conversely, the conversion of nitrate to dinitrogen is hindered by the requirement for extended residence times to achieve near-complete nitrate removal, representing a considerable obstacle to efficient implementation.

RESEARCH PROGRESS ON C-N COUPLING REDUCTION

Beyond the straightforward removal of nitrate from wastewater, integrating nitrate reduction at low concentrations with carbon dioxide reduction (CO_2RR) to synthesize high-value products broadens the scope of applications for electrochemical wastewater management. Moreover, coupling N with C through electroreduction serves as a nexus between NO_3RR and CO_2RR, offering valuable perspectives on sustainable electrochemical synthesis.[38] As early as 1990-2000s, Shibata et al. first investigated the electrochemical synthesis of urea by the co-reduction of CO_2 and nitrate on a series of metal-based gas-diffusion electrodes.[39,40] The findings indicated that the Faraday efficiency of urea formation from nitrate could potentially reach up to 35% when using zinc electrodes in this C-N coupling process.

However, at that time, the mechanism for the C-N coupling reduction is blurred. With the development of characterization techniques and computational simulations, the corresponding reaction mechanism has raised great interest among researchers. Due to the involvement of the C-N compound in the co-reduction reaction, the mechanism is much more complicated than CO_2RR and NO_3RR and could lead to a large amount of possible intermediates and end-products as shown in Figure 4.[41]

The electrochemical C-N coupling reaction contains a series of pathways, which could be categorized as electrochemical steps and chemical steps. For both the CO_2 molecules and NO_3^- ions, the first step is the adsorption on the catalyst surface, a crucial step that significantly influences the reaction rates. Following the adsorption, the adsorbed species, denoted as $^*NO_3$ and $^*CO_2$, are electrochemically reduced to specific intermediates. These intermediates subsequently undergo chemical coupling steps to form the desired organonitrogen compounds. There have been studies that revealed that the C-N bond formation is the critical step where the N-containing nucleophilic intermediates would attack the active center of the CO_2RR intermediates. However, this also proved to be the rate-determining step of the co-reduction process due to the slow kinetics despite the thermodynamic favorability.

Generally, the main products of electrochemical C-N coupling include urea, amines, and amides.[12] Among them, urea is the most widely investigated end-product considering its market value. As early as 1995, Shibata et al. pioneered the concept and explored the feasibility of electrocatalytic urea synthesis using CO_2 and NO_3^- as reactants, laying the groundwork for subsequent research in the field.[42] However, considering the complicated reaction pathways, achieving high selectivity and efficiency is difficult, as competing reactions can produce unwanted byproducts. Effective catalysts are crucial for enhancing the process toward urea, and ongoing research focuses on developing catalysts that operate under mild conditions with high activity. Zhang et al. reported the bonded Fe-Ni pairs as efficient active sites for C-N coupling and finally achieved the urea yield rate of 20.2 mmol h^{-1} g^{-1} with the Faraday efficiency of 17.8%. Wei et al. synthesized the oxygen vacancy induced CeO_2 and achieved the highest urea yield rate of 943.6 mg h^{-1} g^{-1} at around 40 mA cm^{-2}. However, the Faraday efficiency under this circumstance is only 1%.[43] More recently, with great emphasis focused on this area, there has been prominent enhancement in Faraday efficiency under small current densities. Ye et al. reported a novel metal/hydroxide heterojunction strategy to construct Ag-CuNi$(OH)_2$ composite catalysts, finally realizing a urea yield rate of 25.6 mmol g^{-1} h^{-1} with FE of 46.1% (around 6–8 mA cm^{-2}).[44] The strongly coupled metal/hydroxide heterojunction interface is capable of binding two different sites to activate carbon dioxide molecules and nitrate and promotes the coupling of *CO (adsorbed on Ag sites) and $*NH_2$ (adsorbed on CuNi$(OH)_2$). Chen et al. reported an amorphous bismuth-tin oxide nanosheets for urea synthesis through C-N coupling.[45] The optimized orbital symmetry of the C($*CO_2$)-containing and N($*NO_2$)-containing intermediates significantly improves the Faraday efficiency of urea production to 78.36% at −0.4 V.

Despite promising, the study on the C-N coupling reduction is still in its initial stage facing with severe obstacles on the low production rate. To date, the urea yield rate remains on the microgram level per hour, primarily due to the presence of various byproducts. Typically, at a current density exceeding 10 mA cm^{-2}, the Faraday efficiency falls below 20%, indicating the urgent need for advancements to improve efficiency. For future development in pursuit of efficient production, strategies could be concluded from two aspects: a) modulating the active sites through innovative catalyst design and b) engineering the intermediates of the local environment.[46,47]

In summary, the C-N coupling reduction is promising for nitrate treatment originating from wastewater, alongside facilitating the synthesis of value-added organonitrogen compounds. However, the efficiency of this reaction is far from a practical requirement and the technology has not evolved the conversion of nitrate at wastewater concentration level. Consequently, substantial research and development efforts are imperative to advance this conversion strategy at this stage.

FEASIBILITY DISCUSSION IN PRACTICAL APPLICATION

Beyond the theoretical viability of the aforementioned nitrate removal strategies, further discussions encompassing the nitrate concentration from various sources, reactor design and energy sources, and so forth should be taken into consideration aiming at practical application.

The concentration of nitrates in wastewater varies significantly depending on the source of the wastewater, reflecting the diverse activities and processes that contribute to nitrate pollution. In industry, the generated nitrate pollutants could even reach the N-NO_3^- concentration of over 500 mg L^{-1} during the production of electronic components, explosives, and fertilizers.[48] Additionally, steel factory is another significant pollutant source of nitrate and even after the pre-treatment in the factory itself, the discharged wastewater normally contains the high N-NO_3^- concentration of 600–1000 mg L^{-1}. Meanwhile, the concentration of nitrate in municipal wastewater and agricultural runoff is much lower compared to those present in industry. For municipal wastewater, the common concentration of nitrate is within the N-NO_3^- range of 10–200 mg L^{-1}.[49] In the polluted natural water body, this value could be detected around 3–5 mg L^{-1} and reach over 20 mg L^{-1} in some typical irrigated areas, which is higher than the water disposal limitation of 10 mg L^{-1} by China and United States.[50,51] However, only 1–2 mg L^{-1} of N-NO_3^- would trigger severe algal blooms and cause human health concerns.[18] Therefore, reducing nitrate levels in wastewater is both a necessary and viable measure for practical environmental management.

Shedding light on the practical conversion of nitrates, the development of a suitable reactor is another crucial factor in feasibility discussions. Typically, at the laboratory scale, single-chamber and H-cell reactors with chamber volumes ranging from 30 to 200 mL are used for nitrate conversion (Figure 5A). However, this design has limitations on mass transfer and is not suitable for wastewater management at an industrial scale. So far, two main types of reactors have been documented and utilized in various situations. The first type is the flow-by reactor, which ensures a continuous and adequate supply of nitrate for the conversion process. This type of reactor is suitable for relatively high concentrations of nitrate and is designed for the conversion of valuable products. For instance, Zhang et al. developed a Bi–FeS2 catalyst, which was strategically loaded onto a gas diffusion electrode (GDE) within a flow cell. This setup achieved a near-100% FE for ammonia and a high ammonia yield rate of 83.7 mg h^{-1} cm^{-2} at a current density of 1023.2 mA cm^{-2}. Additionally, it demonstrated excellent long-term durability, sustaining continuous electrolysis for over 100 h.[52] Xu et al. designed a bipolar membrane reactor for the continuous electrosynthesis of ammonia from 2000 ppm nitrate (Figure 5C).[53] To achieve ionic equilibrium, a bipolar membrane nitrate reduction process was proposed, and the hydrolysis dissociation sites were increased by constructing a three-dimensional physically interlocking interface for the bipolar membrane in this study. Moreover, based on the flow-by structure, a scaling-up reactor has been developed with the electrolyte volume of 500 L by Zheng et al. (Figure 5D).[54] The other structure type is the flow-through reactor, which is perfect for realizing the electrofiltration of ultra-low nitrate concentration. Wang et al. reported a flow-through electrofiltration reactor via an electrified membrane incorporated with Cu single-atom catalysts for nitrate reduction to nitrogen gas (Figure 5B).[18] Compared with the flow-by reactor, the reported flow-through electrofiltration presented significant enhancement in dinitrogen selectivity and finally realized the near-complete removal of N-NO_3^- concentration at 10 mg L^{-1} with a residence time of only 10 s. This superior performance is due to the increased adsorption and transportation of *NO intermediate, combined with a balanced supply of atomic hydrogen through hydrogen dissociation during the electrofiltration. In addition, both two types of reactors are scalable, enabling the configurations with hundreds of liters or even cubic meters in size.

Furthermore, renewable energy as a power source has emerged as a dependable and cost-effective source for driving large-scale electrochemical nitrate management.[55] Utilizing renewable energy for the electrochemical nitrate management offers numerous benefits, including enhanced environmental sustainability by reducing greenhouse gas emissions and aligning with climate change initiatives. It is increasingly cost-effective due to declining renewable energy prices, which lowers operational expenses and makes large-scale implementation more feasible. Renewable energy also promotes energy

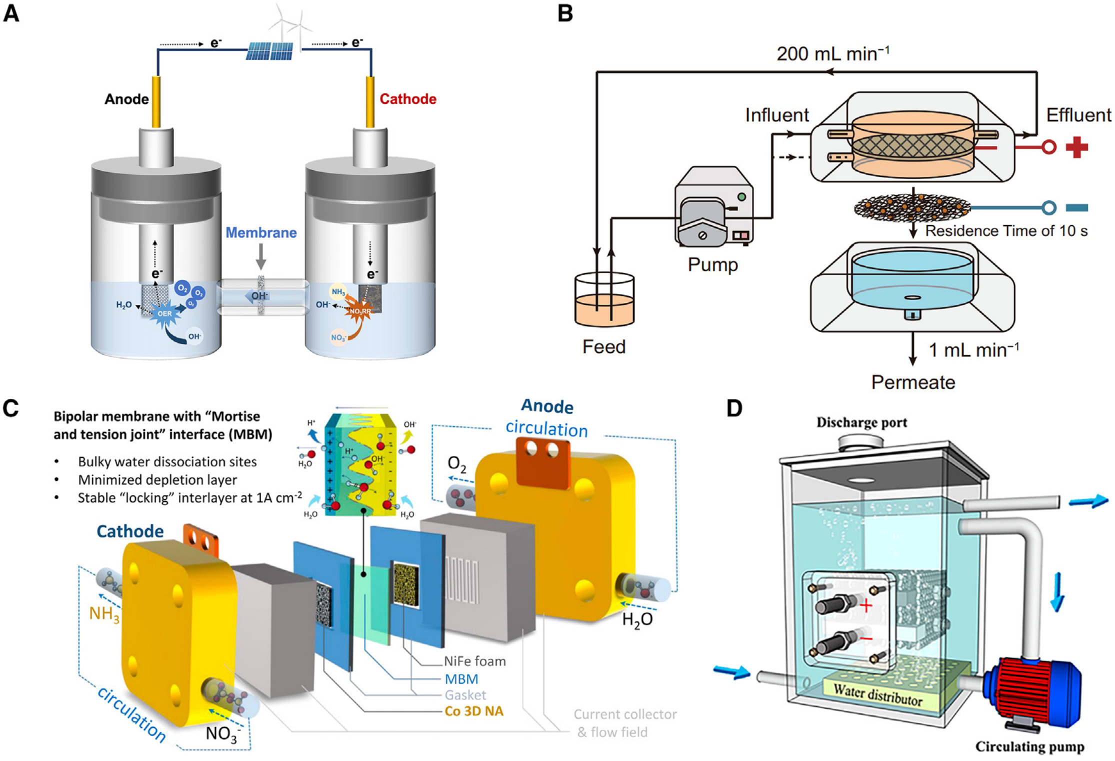

Figure 5. Reported practical application of NO_3RR

The schematic illustration of (A) H-cell reactor and (B) flow-through electrofiltration reactor. Copyright 2023, the authors.[18]
(C) Bipolar membrane reactor for ammonia electrosynthesis in flow mode. Copyright 2023, Springer Nature.[53]
(D) Scaling-up flow-by prototype reactor.[54] Copyright 2021, American Chemical Society.

independence, reducing reliance on imported fuels and protecting against market volatility. Its scalability and flexibility allow for tailored solutions to meet specific demands. Additionally, it supports regulatory compliance and can attract incentives, while improving public perception and corporate responsibility by demonstrating a commitment to sustainability. Continuous technological advancements further enhance the reliability and efficiency of renewable energy systems, making them an ideal choice for nitrate management.

In addition, the large-scale synthesis and separation of ammonia from nitrate reduction in wastewater treatment is a challenge. Once produced, ammonia is typically mixed with other wastewater constituents in a dilute form, which requires additional separation processes such as distillation or membrane separation, which can be energy intensive and costly. The integration of such conversion processes into existing wastewater treatment systems requires careful consideration of flow rates, concentrations, and compatibility with other processes. Economic viability depends on balancing the cost of conversion and separation against the value of recovered ammonia, while also assessing the environmental impact, including energy consumption and emissions. In addition, due to the hazardous nature of ammonia, compliance and safety measures are critical. Despite the promise of ammonia from nitric acid technology, significant challenges related to efficiency, separation, integration, and cost must also be addressed for ammonia from nitric acid to be a practical and sustainable solution, which will require ongoing research and technological advances.

Besides, there has been only a scarcity of economic analyses focusing on energy consumption by researchers, making it challenging to assess the marketing feasibility. Consequently, it is imperative to integrate evaluations of energy costs and their respective energy sources into the forthcoming phase of development.

CONCLUSION AND OUTLOOKS

Electroreduction of low-concentration nitrate has emerged as a promising strategy for wastewater management. In this perspective article, we overviewed the recent progress in nitrate reduction including direct nitrate reduction and C-N coupling reduction, both of which have captivated the scientific community. The comparison of the evaluation indexes of the three main strategies is shown in Figure 6.

From a mechanistic perspective, the electroreduction of low-concentration nitrate is not only feasible but also characterized by a complex and nuanced mechanism, which deserves extensive investigation. Despite the promising theoretical and experimental insights, the practical application of nitrate reduction in wastewater treatment is still in its developmental phase. Of the various techniques under investigation, the electrochemical

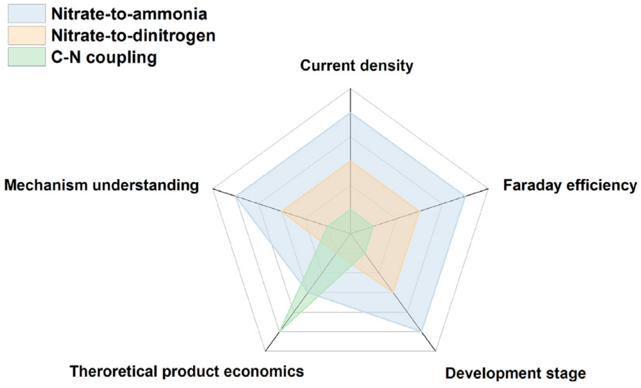

Figure 6. Radar map of the evaluation indexes for low concentration nitrate conversion strategies

conversion of nitrate to ammonia is the most advanced with respect to potential real-world application. On one hand, the efficiency of nitrate reduction to ammonia has reached over 90% along with the ammonia yield rate as high as gram-level in previous reports. Meanwhile, there have been works investigating the novel-designed reactor suitable for large-scale ammonia production while maintaining the satisfactory conversion rate. The controversies of this process are on the extra cost of separation and purification of ammonia from the electrolyte. For the next stage, it is critical to take the reprocessing into consideration. Moreover, a thorough and professional assessment of the economic aspects is crucial, encompassing detailed estimations of energy consumption costs, catalyst usage, reactor construction, and other related expenses. In contrast, the nitrate-to-dinitrogen process and C-N coupling reduction are still at the very early stage in the laboratory. Both reactions encounter significant kinetic challenges, leading to insufficient efficiency and conversion rates. To reach the requirement of practical application, the energy efficiency should reach at least 60% at 300 mA cm^{-2} according to the target of the U.S. Department of Energy (DOE). Although there have been some studies reporting high Faraday efficiency recently, they all sacrifice the current density thus leading to extremely low yield rate correspondingly. Therefore, future research and development efforts should aim to enhance the performance of the reactions through the optimization of activity and selectivity of catalysts, or the modification of electrode-electrolyte interface to steer the reactions toward desired directions.

In conclusion, while the current research on the electroreduction of low-concentration nitrate is insufficient to fully meet the practical demands of wastewater management, there is significant potential for future advancements. Continuous progress in understanding the underlying mechanisms and developing innovative technologies could overcome existing barriers, making real-world applications more feasible. Researchers are focusing on improving catalyst efficiency, selectivity, and stability, which are crucial for enhancing the overall process. Additionally, integrating advanced separation techniques and optimizing system designs could reduce costs and energy consumption, making the process more economically viable. As these developments unfold, they are expected to lead to breakthroughs in wastewater management, offering new perspectives and opportunities for technological transformation. This progress could significantly impact the global electrochemistry field, driving sustainable practices and contributing to environmental conservation. The optimism surrounding these advancements suggests a promising future where nitrate electroreduction plays a key role in addressing global wastewater challenges.

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AUTHOR CONTRIBUTIONS

Liang An proposed the topic of the review. **Xiao Zhang** proposed the outline of the review. **Kouer Zhang** drafted the article. All authors contributed to the editing of the article.

DECLARATION OF INTERESTS

The authors declare no conflict of interest.

REFERENCES

1. Wang, Y., Wang, C., Li, M., Yu, Y., and Zhang, B. (2021). Nitrate electroreduction: mechanism insight, *in situ* characterization, performance evaluation, and challenges. Chem. Soc. Rev. *50*, 6720–6733.
2. Jiang, M., Zhu, M., Wang, M., He, Y., Luo, X., Wu, C., Zhang, L., and Jin, Z. (2023). Review on Electrocatalytic Coreduction of Carbon Dioxide and Nitrogenous Species for Urea Synthesis. ACS Nano *17*, 3209–3224.
3. Tang, W., Kovalsky, P., He, D., and Waite, T.D. (2015). Fluoride and nitrate removal from brackish groundwaters by batch-mode capacitive deionization. Water Res. *84*, 342–349.
4. Sinha, E., Michalak, A.M., and Balaji, V. (2017). Eutrophication will increase during the 21st century as a result of precipitation changes. Science *357*, 405–408.
5. Hell, F., and Liebminger, L.A. (2024). In Handbook of Water and Used Water Purification (Springer), pp. 387–403.
6. Huno, S.K.M., Rene, E.R., van Hullebusch, E.D., and Annachhatre, A.P. (2018). Nitrate removal from groundwater: a review of natural and engineered processes. J. Water Supply Res. Technol. - Aqua *67*, 885–902.
7. Abayie, S.O., and Leiviskä, T. (2022). Removal of nitrate from underground mine waters using selective ion exchange resins. J. Environ. Chem. Eng. *10*, 108642.
8. Aslan, S., and Türkman, A. (2004). Biological denitrification of drinking water using various natural organic solid substrates. Water Sci. Technol. *48*, 489–495.
9. Zhang, K., Liu, Y., Pan, Z., Xia, Q., Huo, X., Esan, O.C., Zhang, X., and An, L. (2024). Cu-based catalysts for electrocatalytic nitrate reduction to ammonia: fundamentals and recent advances. EES Catalysis *2*, 727–752.
10. van Langevelde, P.H., Katsounaros, I., and Koper, M.T. (2021). Electrocatalytic Nitrate Reduction for Sustainable Ammonia Production. Joule *5*, 290–294.
11. Wang, Y., Yu, Y., Jia, R., Zhang, C., and Zhang, B. (2019). Electrochemical synthesis of nitric acid from air and ammonia through waste utilization. Natl. Sci. Rev. *6*, 730–738.
12. Li, J., Zhang, Y., Kuruvinashetti, K., and Kornienko, N. (2022). Construction of C–N bonds from small-molecule precursors through heterogeneous electrocatalysis. Nat. Rev. Chem *6*, 303–319.

13. Ye, Y., Li, Z., Ding, S., Fu, J., Liu, H., and Zhu, W. (2023). Synergistic treatment of carbon dioxide and nitrogen-containing wastewater by electrochemical C-N coupling. iScience *26*, 107009.

14. Rosca, V., Duca, M., de Groot, M.T., and Koper, M.T.M. (2009). Nitrogen Cycle Electrocatalysis. Chem. Rev. *109*, 2209–2244.

15. Liu, J.-X., Richards, D., Singh, N., and Goldsmith, B.R. (2019). Activity and Selectivity Trends in Electrocatalytic Nitrate Reduction on Transition Metals. ACS Catal. *9*, 7052–7064.

16. De Groot, M., and Koper, M. (2004). The influence of nitrate concentration and acidity on the electrocatalytic reduction of nitrate on platinum. J. Electroanal. Chem. *562*, 81–94.

17. Garcia-Segura, S., Lanzarini-Lopes, M., Hristovski, K., and Westerhoff, P. (2018). Electrocatalytic reduction of nitrate: Fundamentals to full-scale water treatment applications. Appl. Catal. B Environ. *236*, 546–568.

18. Wang, X., Wu, X., Ma, W., Zhou, X., Zhang, S., Huang, D., Winter, L.R., Kim, J.-H., and Elimelech, M. (2023). Free-standing membrane incorporating single-atom catalysts for ultrafast electroreduction of low-concentration nitrate. Proc. Natl. Acad. Sci. USA *120*, e2217703120.

19. Xu, B., Chen, Z., Zhang, G., and Wang, Y. (2021). On-Demand Atomic Hydrogen Provision by Exposing Electron-Rich Cobalt Sites in an Open-Framework Structure toward Superior Electrocatalytic Nitrate Conversion to Dinitrogen. Environ. Sci. Technol. *56*, 614–623.

20. Martínez, J., Ortiz, A., and Ortiz, I. (2017). State-of-the-art and perspectives of the catalytic and electrocatalytic reduction of aqueous nitrates. Appl. Catal. B Environ. *207*, 42–59.

21. Zhang, G., Li, X., Chen, K., Guo, Y., Ma, D., and Chu, K. (2023). Tandem electrocatalytic nitrate reduction to ammonia on MBenes. Angew. Chem. Int. Ed. *62*, e202300054.

22. Zhang, G., Wang, F., Chen, K., Kang, J., and Chu, K. (2024). Atomically dispersed Sn confined in FeS_2 for Nitrate-to-Ammonia Electroreduction. Adv. Funct. Mater. *34*, 2305372.

23. Chen, F.-Y., Wu, Z.-Y., Gupta, S., Rivera, D.J., Lambeets, S.V., Pecaut, S., Kim, J.Y.T., Zhu, P., Finfrock, Y.Z., Meira, D.M., et al. (2022). Efficient conversion of low-concentration nitrate sources into ammonia on a Ru-dispersed Cu nanowire electrocatalyst. Nat. Nanotechnol. *17*, 759–767.

24. Zhang, K., Sun, P., Huang, Y., Tang, M., Zou, X., Pan, Z., Huo, X., Wu, J., Lin, C., and Sun, Z. (2024). Electrochemical nitrate reduction to ammonia on CuCo nanowires at practical level. Adv. Funct. Mater. *34*, 2405179.

25. Dou, F., Guo, F., Li, B., Zhang, K., Graham, N., and Yu, W. (2024). Pulsed electro-catalysis enables effective conversion of low-concentration nitrate to ammonia over Cu2O@Pd tandem catalyst. J. Hazard Mater. *472*, 134522.

26. Zhu, X., Ma, C., Wang, Y.-C., Qu, K., Song, L., Wang, J., Gong, Y., Liu, X., Zhang, J., Lu, Q., and Wang, A.L. (2024). Mott–Schottky contact synergistically boosts the electroreduction of nitrate to ammonia under low-nitrate concentration. Energy Environ. Sci. *17*, 2908–2920.

27. Yuan, M., Sun, J., Wu, Y., Zheng, M., Sheng, C., Wu, C., and Wang, Q. (2024). Enhanced electroreduction of low-concentration nitrate using a Cu-Pd bimetallic cathode system: Performance evaluation, mechanism analysis, and potential applications. J. Environ. Chem. Eng. *12*, 113031.

28. Lu, B., Liu, Q., and Chen, S. (2020). Electrocatalysis of Single-Atom Sites: Impacts of Atomic Coordination. ACS Catal. *10*, 7584–7618.

29. Liu, L., and Corma, A. (2018). Metal Catalysts for Heterogeneous Catalysis: From Single Atoms to Nanoclusters and Nanoparticles. Chem. Rev. *118*, 4981–5079.

30. Wu, Z.-Y., Karamad, M., Yong, X., Huang, Q., Cullen, D.A., Zhu, P., Xia, C., Xiao, Q., Shakouri, M., Chen, F.-Y., et al. (2021). Electrochemical ammonia synthesis via nitrate reduction on Fe single atom catalyst. Nat. Commun. *12*, 2870.

31. Xue, Y., Yu, Q., Ma, Q., Chen, Y., Zhang, C., Teng, W., Fan, J., and Zhang, W.-X. (2022). Electrocatalytic Hydrogenation Boosts Reduction of Nitrate to Ammonia over Single-Atom Cu with Cu(I)-N_3C_1 Sites. Environ. Sci. Technol. *56*, 14797–14807.

32. Xiao, C., Guo, Y., Sun, J., Guo, T., Jia, X., Guo, S., Wu, G., Sun, Y., Yao, Z., and Liu, Y. (2024). Efficient electrocatalytic reduction of nitrate to ammonia at low concentration by copper-cobalt oxide nanowires with shell–core structure. Nano Res. *17*, 5087–5094.

33. Huang, Y., He, C., Cheng, C., Han, S., He, M., Wang, Y., Meng, N., Zhang, B., Lu, Q., and Yu, Y. (2023). Pulsed electroreduction of low-concentration nitrate to ammonia. Nat. Commun. *14*, 7368.

34. Xu, H., Chen, J., Zhang, Z., Hung, C.T., Yang, J., and Li, W. (2023). In situ confinement of ultrasmall metal nanoparticles in short mesochannels for durable electrocatalytic nitrate reduction with high efficiency and selectivity. Adv. Mater. *35*, 2207522.

35. Daiyan, R., Tran-Phu, T., Kumar, P., Iputera, K., Tong, Z., Leverett, J., Khan, M.H.A., Asghar Esmailpour, A., Jalili, A., Lim, M., et al. (2021). Nitrate reduction to ammonium: from CuO defect engineering to waste NO_x-to-NH_3economic feasibility. Energy Environ. Sci. *14*, 3588–3598.

36. Feng, T., Wang, J., Wang, Y., Yu, C., Zhou, X., Xu, B., László, K., Li, F., and Zhang, W. (2022). Selective electrocatalytic reduction of nitrate to dinitrogen by Cu2O nanowires with mixed oxidation-state. Chem. Eng. J. *433*, 133495.

37. Xiong, Y., Wang, Y., Zhou, J., Liu, F., Hao, F., and Fan, Z. (2024). Electrochemical nitrate reduction: ammonia synthesis and the beyond. Adv. Mater. *36*, 2304021.

38. Lv, C., Liu, J., Lee, C., Zhu, Q., Xu, J., Pan, H., Xue, C., and Yan, Q. (2022). Emerging p-Block-Element-Based Electrocatalysts for Sustainable Nitrogen Conversion. ACS Nano *16*, 15512–15527.

39. Shibata, M., Yoshida, K., and Furuya, N. (1998). Electrochemical Synthesis of Urea at Gas-Diffusion Electrodes: IV. Simultaneous Reduction of Carbon Dioxide and Nitrate Ions with Various Metal Catalysts. J. Electrochem. Soc. *145*, 2348–2353.

40. Shibata, M., and Furuya, N. (2003). Simultaneous reduction of carbon dioxide and nitrate ions at gas-diffusion electrodes with various metallophthalocyanine catalysts. Electrochim. Acta *48*, 3953–3958.

41. Zheng, M., Ma, H., Li, Z., Yu, H., Nie, L., Ye, C., Chen, X., and Wang, J. (2024). Theoretical insights on C-N coupling mechanism and guidance for screening the catalysts of electrocatalytic urea synthesis by descriptors. Appl. Catal. B Environ. *342*, 123366.

42. Shibata, M., Yoshida, K., and Furuya, N. (1995). Electrochemical synthesis of urea on reduction of carbon dioxide with nitrate and nitrite ions using Cu-loaded gas-diffusion electrode. J. Electroanal. Chem. *387*, 143–145.

43. Wei, X., Wen, X., Liu, Y., Chen, C., Xie, C., Wang, D., Qiu, M., He, N., Zhou, P., Chen, W., et al. (2022). Oxygen Vacancy-Mediated Selective C–N Coupling toward Electrocatalytic Urea Synthesis. J. Am. Chem. Soc. *144*, 11530–11535.

44. Ye, W., Zhang, Y., Chen, L., Wu, F., Yao, Y., Wang, W., Zhu, G., Jia, G., Bai, Z., Dou, S.X., et al. (2024). A Strongly Coupled Metal/Hydroxide Heterostructure Cascades Carbon Dioxide and Nitrate Reduction Reactions toward Efficient Urea Electrosynthesis. Angew. Chem. Int. Ed. *63*, e202410105.

45. Chen, X., Lv, S., Gu, H., Cui, H., Liu, G., Liu, Y., Li, Z., Xu, Z., Kang, J., Teobaldi, G., et al. (2024). Amorphous Bismuth–Tin Oxide Nanosheets with Optimized C–N Coupling for Efficient Urea Synthesis. J. Am. Chem. Soc. *146*, 13527–13535.

46. Hu, Q., Zhou, W., Qi, S., Huo, Q., Li, X., Lv, M., Chen, X., Feng, C., Yu, J., and Chai, X. (2024). Pulsed co-electrolysis of carbon dioxide and nitrate for sustainable urea synthesis. Nat. Sustain. *7*, 442–451.

47. Zhao, Y., Ding, Y., Li, W., Liu, C., Li, Y., Zhao, Z., Shan, Y., Li, F., Sun, L., and Li, F. (2023). Efficient urea electrosynthesis from carbon dioxide and nitrate via alternating Cu–W bimetallic C–N coupling sites. Nat. Commun. *14*, 4491.

48. Fernández-Nava, Y., Maranon, E., Soons, J., and Castrillón, L. (2008). Denitrification of wastewater containing high nitrate and calcium concentrations. Bioresour. Technol. *99*, 7976–7981.

49. Glass, C., and Silverstein, J. (1999). Denitrification of high-nitrate, high-salinity wastewater. Water Res. *33*, 223–229.

50. Xu, A., Wu, Y.-H., Chen, Z., Wu, G., Wu, Q., Ling, F., Huang, W.E., and Hu, H.-Y. (2020). Towards the new era of wastewater treatment of China: Development history, current status, and future directions. Water Cycle *1*, 80–87.

51. Cotruvo, J.A., and Regelski, M. (2017). In Safe Drinking Water Act (CRC Press), pp. 29–34.

52. Zhang, G., Wang, G., Wan, Y., Liu, X., and Chu, K. (2023). Ampere-Level Nitrate Electroreduction to Ammonia over Monodispersed Bi-Doped FeS_2. ACS Nano *17*, 21328–21336.

53. Xu, Z., Wan, L., Liao, Y., Pang, M., Xu, Q., Wang, P., and Wang, B. (2023). Continuous ammonia electrosynthesis using physically interlocked bipolar membrane at 1000 mA cm^{-2}. Nat. Commun. *14*, 1619.

54. Zheng, W., Zhu, L., Yan, Z., Lin, Z., Lei, Z., Zhang, Y., Xu, H., Dang, Z., Wei, C., and Feng, C. (2021). Self-activated Ni cathode for electrocatalytic nitrate reduction to ammonia: from fundamentals to scale-up for treatment of industrial wastewater. Environ. Sci. Technol. *55*, 13231–13243.

55. Badwal, S.P., Giddey, S.S., Munnings, C., Bhatt, A.I., and Hollenkamp, A.F. (2014). Revisiting 30 years of biofunctionalization and surface chemistry of inorganic nanoparticles for nanomedicine. Front. Chem. *2*, 48.