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REVIEW ARTICLE

Recent innovations in urea synthesis via electrochemical C-N coupling reaction: insights and perspectives

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Abstract
Among nitrogen-based fertilizers, urea is the most important and dominant candidate, with an approximate share of 50% in the agriculture market, utilizing about 2% of the worldwide energy for its industrial-scale production. In turn, the process accounts for about 3% of the carbon dioxide (CO_2) emissions globally, which subsequently contributes to the energy crisis, greenhouse gas emissions, and global warming. These carbon emission figures imply a strict and urgent need for the development of alternative, sustainable, and efficient methodologies for environmentally friendly urea production. The electrochemical C-N coupling approach for urea synthesis is a sustainable alternative approach being explored to slowly replace the existing energy-consuming industrial urea production process. The electrochemical urea synthesis is currently in its nascent stage, and at present this technology is far from industrial-scale application, and hence, herein we present this review, which highlights the mechanism for urea synthesis, recent breakthroughs and developments, while highlighting the challenges associated with electrochemical urea synthesis. In order to further enhance reaction efficiency and selectivity, electrocatalysts play a vital part in the electrochemical urea production pathways; however, a number of constraints, such as the need for superior catalyst performance, understanding of complicated chemical pathways, and process scalability for industrial use still need to be conquered. This review highlights research on the recent developments in electrochemical urea synthesis and sheds light on the requirements for a feasible process to give guidance and directions for future research work.

Keywords Green urea · Electrochemical C-N coupling · Nitrogen reduction reactions · Green chemicals · Frustrated lewis pairs · Sustainable development

Introduction

The rapid expansion of the global economy, fueled by industrialization—especially in the chemical sector has heavily depended on fossil fuels. These non-renewable energy sources serve as the primary feedstock for various industrial processes and as a significant energy source for global production (Kohlhaas et al. 2024). However, this reliance has resulted in the accelerated depletion of fossil fuel reserves, raising concerns about resource scarcity and energy security in the future.

Simultaneously, the widespread combustion of fossil fuels generates substantial quantities of carbon-based emissions, primarily CO_2, which are released into the atmosphere. These emissions significantly contribute to global warming by enhancing the greenhouse effect, which results in increase in global temperatures leading to melting of polar ice caps, rising sea levels, and an increased frequency of extreme weather events such as hurricanes, droughts, and heatwaves (De Luna et al. 2019). Furthermore, human activities, such as the discharge of industrial waste and the excessive use of fertilizers in agriculture, have exacerbated the release of pollutants into the environment. Industrial effluents and runoff from agricultural fields often contain high concentrations of nitrogen-based contaminants, including nitrite (NO_2^-) and nitrate (NO_3^-), which upon accumulation in underground water sources, leads to significant contamination (Duca and Koper 2012). Elevated levels of nitrates and nitrites in drinking water can pose serious health risks to humans, including methemoglobinemia, commonly known as "blue baby syndrome," which impairs oxygen transport in the blood. Prolonged exposure is also associated with an increased risk of cancer

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and other chronic illnesses. In addition to the risks posed to human health, nitrogen pollution presents a significant threat to aquatic ecosystems. Elevated concentrations of nitrogen compounds stimulate eutrophication, a process that leads to the excessive growth of algae and aquatic plants. This overgrowth depletes oxygen levels in the water, creating hypoxic or "dead zones" where aquatic life cannot survive. Such environmental degradation has cascading effects on biodiversity, fisheries, and the livelihoods of communities that depend on aquatic resources.

Given the dual challenges of environmental degradation and resource depletion, it is imperative to develop innovative strategies for sustainable energy and pollution mitigation. One effective approach involves converting CO_2 and nitrogen (N_2) as well as nitrogen-based pollutants into high-value chemical products. This strategy not only addresses the urgent need to reduce harmful emissions and contaminants but also provides a pathway for producing sustainable alternatives to traditional fossil fuel-derived chemicals. By leveraging advancements in catalytic processes, green chemistry, and the integration of renewable energy, this approach has the potential to promote both environmental and economic sustainability.

From its inception in 1922, the Bosch-Meiser process has historically been the main technology till now to industrially produce urea. This industrial process involves the reaction of ammonia (NH_3) typically produced from Haber–Bosch with CO_2 at elevated temperature and pressure conditions where ammonium carbamate (NH_4HCO_2) is observed as an intermediate and the final reaction is observed to be an exothermic reaction resulting in the production of urea and water (Meessen et al. 2014). It is worth noting that the high operating conditions of the Bosch-Meiser and Haber–Bosch processes are quite similar; the Haber–Bosch process is carried out at around 190 °C and pressures of 140–175 bar, while the Bosch-Meiser process requires temperatures of 400–650 °C and pressures of 100–400 bar. In the final stage, this urea thus produced, is dried up and then used as a final product in a number of industries, including fertilizer, chemicals, etc.

Considering its ambient operating conditions and nearly carbon-free emissions as shown in Fig. 1, the alternative electrochemical urea synthesis technique is the leading replacement approach for the Haber–Bosch and Bosch-Meiser process (Orella et al. 2018).

The very initial studies on electrochemical urea synthesis were carried out by Furuya and coworkers in 1995. The researchers used Cu-loaded gas-diffusion electrodes as working electrodes and synthesized urea by co-reducing CO_2 and NO_3^-/NO_2^- electrochemically (Shibata et al. 1995). Subsequently, Furuya's group exploited metal-phthalocyanine (M-Pc)-based electrocatalysts for the

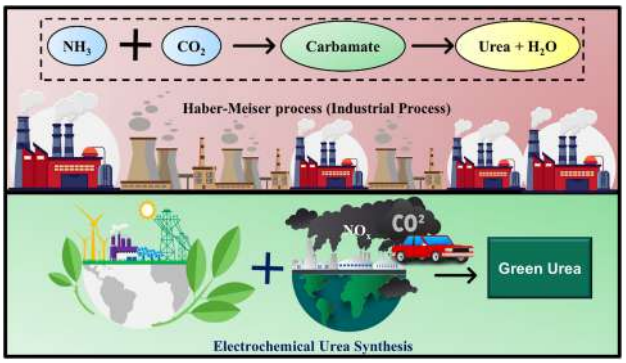

Fig. 1 Depicts the schematic illustration of difference between Haber Meiser process and electrochemical urea synthesis

electrochemical synthesis of urea, where the Ni-Pc catalyst displayed an exceptional Faradaic efficiency (FE) of 40% (Shibata and Furuya 2001, 2003). Although a number of studies have been carried out during the period 1995–2019, electrochemical urea synthesis started gaining attention starting from around 2020 (Xiang et al. 2012). For instance, in the year 2016, Köleli F. et al. investigated the simultaneous electrocatalytic reduction of CO_2 and N_2 in an aqueous 0.1 M Li_2SO_4/0.03 M H^+ solution at 60 bar using platinum electrodes coated with polyaniline and polypyrrole (Kayan and Köleli 2016). In another study carried out in 2017, Shin W et. al. utilized a TiO_2-Nafion nanocomposite electrode that effectively converted CO_2 and nitrate ions to urea. The researchers used a mixture of P25 titania and Nafion solution, drop-cast over an indium-doped tin oxide (ITO) electrode and the investigations led to the successful formation of electrochemical urea with a Faradaic efficiency of 40% at − 0.98 V vs. Ag/AgCl in a CO_2-saturated 0.1 M KNO_3 (pH 4.5) solution (Saravanakumar et al. 2017). Upon careful examination, it has come to our attention that a limited number of studies have been carried out on electrochemical urea synthesis from 1995–2019, and the field started evolving starting from 2020 and has seen substantial growth and breakthroughs. Although, few reviews have focused on the development process, catalyst design, and action mechanism for electrocatalytic urea synthesis, this review specifically aims to provide a systematic update of the very recent developments and breakthroughs observed in the C−N coupling reaction in the past five years. It will provide important references for designing highly efficient electrocatalysts and developing strategies for improving performance. The review summarizes progress in electrochemical urea synthesis using CO_2 and different N-sources, advanced catalyst design strategies, and C−N coupling reaction mechanisms under ambient conditions.

Introduction to electrochemical urea formation and understanding the mechanism for electrochemical urea production

There are significant economic and environmental advantages to the revolutionary use of nitrate/nitrites and CO_2 as feedstock for the synthesis of urea. Additionally, the technique substantially reduces dependence on scarce fossil fuel resources and contributes to reducing greenhouse gas emissions, both of which will likely reduce the cost of producing urea (Mukherjee et al. 2022a). However, this process has numerous technical hurdles, especially because of the high chemical stability of N_2 and the huge activation energy barrier of CO_2. Due to differences in their activation energies, intermediate species, reaction pathways, and other characteristics, different reactants argue for different catalysts. For instance, N_2 and CO_2 being less chemically active requires very high bond energies, which are 941 kJ mol^{-1} for the N≡N bond and 806 kJ mol^{-1} for the C═O bond to activate the respective molecules. On the other hand, owing to their low bond energies (204 kJ mol^{-1} for the N═O and 176 kJ mol^{-1} for the N─O bond), nitrogen sources, NO, NO_3^-, and NO_2^-, have high chemical activity. The full reactions toward urea synthesis from different nitrogen sources including NO, NO_2^-, NO_3^- and N_2 are listed in Eqs. 1–4. The redox potentials at which the reactions for electrochemical urea synthesis occur vary depending on the nitrogen source utilized. For the reaction using NO as the nitrogen source, the electrochemical process takes place at approximately − 0.6 to − 1.5 V versus the reversible hydrogen electrode (RHE). When NO_2^- is employed, the reaction occurs within a similar potential range, typically around − 0.2 V, which has been shown to achieve high Faradaic efficiency due to the stabilization of intermediates. In the case of NO_3^-, the required potential is more negative, generally around − 1.0 to − 1.5 V, reflecting the complex 16-electron reduction process involved in converting nitrate to urea.

$$Utilizing\ NO\ as\ Nsource: 2NO + CO_2 + 10H^+ + 10e^- ?NH_2CONH_2 + 3H_2O \quad (1)$$

$$Utilizing\ NO_2^-\ as\ Nsource: 2NO_2^- + CO_2 + 14H^+ + 12e^- \rightarrow NH_2CONH_2 + 5H_2O \quad (2)$$

$$Utilizing\ NO_3^-\ asN\ source: 2NO_3^- + CO_2 + 18H^+ + 16e^- \rightarrow NH_2CONH_2 + 7H_2O \quad (3)$$

$$Utilizing\ N_2\ as\ Nsource: N_2 + CO_2 + 6H^+ + 6e^- \rightarrow NH_2CONH_2 + H_2O \quad (4)$$

Finally, for N_2, which is less soluble in aqueous solutions, the electrochemical reaction is typically conducted at potentials around − 0.8 to − 1.0 V, as it requires overcoming significant kinetic barriers associated with breaking the strong N≡N triple bond. These varying potentials highlight the challenges in optimizing conditions for efficient urea synthesis from different nitrogen sources while minimizing competing side reactions. The reactions mentioned above specifically indicate that the number of electrons being transported influences the chemical step C-N coupling and proton-coupled electron transfer (PCET) in the electrocatalytic process. Thus, the protonation reaction of intermediate species may decrease the selectivity of the C-N coupling, which can affect the overall reaction efficiency. Additionally, the catalyst's ability to stabilize significant chemical intermediates and the byproducts it produces are key factors in the electrocatalytic process's effectiveness (Mukherjee et al. 2022a).

Exploring C-N bond formation: mechanistic pathways in simultaneous co-reduction of nitrogen species (N_2/NO_3^-/NO_2^-) and CO_2

Since nitrogen is the most abundant element in the atmosphere, it provides a particularly attractive source of nitrogen for urea production. Nonetheless, the direct cleavage of N_2 for C − N coupling presents a significant challenge due to the strong bonding strength of the nitrogen triple bond (N≡N), which is approximately 940.95 kJ mol − 1. This electrochemical urea synthesis process generally involves four stages: (1) reactant adsorption, (2) reduction to *CO and *NH_x intermediates, (3) C–N coupling to form NCON, and (4) hydrogenation to produce urea. CO_2 and nitrogen sources (N_2, NO_3^-, NO_2^-) adsorb onto the catalyst surface, and effective adsorption is critical for initiating the reaction. For N_2, adsorption typically occurs in a side-on configuration, which weakens the N≡N bond through electron transfer to antibonding orbitals.

The adsorption of CO_2 varies depending on the catalyst used, with common intermediates such as *COOH or *CO formed during the reduction process. In the subsequent step, the adsorbed CO_2 is reduced to *CO, a crucial intermediate. This step competes with further reduction to methanol (CH_3OH) or methane (CH_4). Simultaneously, nitrogen from various sources is reduced through different intermediates, including N_2 to *N_2H or *NH_2 intermediates, NO_2^-/NO_3^- to *NH_2 or *NO_2 intermediates, and NO is reduced to *NH_2 via *NHO and *NHOH intermediates. In the later stages, C-N coupling occurs, resulting in the formation of *NCON. The coupling of *CO (derived from CO_2) and *NH_2 intermediates generates NCON, a crucial precursor for urea. For instance, on Cu-based catalysts, coupling takes place between *CO and *NH_2 (Cao et al.

2024). Theoretical studies suggest that this coupling is thermodynamically favoured when the intermediates are spatially close on the catalyst surface. In the final stages, the hydrogenation of the intermediates leads to electrochemical urea formation. Hydrogenation may occur via a distal pathway, which involves the sequential protonation of the distal N atom in NCON, or through an alternating pathway, wherein protonation alternates between N atoms, forming intermediates such as *$CONH_2$ before the final release of urea. The detailed mechanism for electrochemical urea synthesis from N_2 with CO_2 as well as Nitrate/Nitrite is depicted in Figs. 2 and 3 respectively. Additionally, it is important to note that the rate-determining step often involves the protonation of NCON intermediates, requiring energy inputs of approximately 1.58 eV.

Recent developments and breakthroughs in the electrochemical C-N coupling

The field of electrochemical urea synthesis has seen significant advancements over the past five years, with researchers developing various catalysts to improve efficiency and production rates. Therefore, many research works proposed different strategies, including vacancy engineering on metal-based oxides, metal doping, defect engineering, controlled atomic spacing, etc., on the surface to promote electrocatalytic co-reduction of CO_2 and NO_x for urea synthesis.

For example, starting from 2020, Feng Y. et al. introduced Te-Pd NCs as an electrocatalyst for urea synthesis, which operates to its fullest at -1.1 V vs. RHE with a Faradaic efficiency of 12.2% using nitrite as the nitrogen source as shown in Fig. 4. This electrocatalyst showed excellent activity as well as Faradaic efficiency in both the H-cell and flow cell system, achieving a noteworthy production rate of 0.95 wt% of urea in the solution (Feng et al. 2020). Later in 2021, several promising electrocatalysts towards urea synthesis were explored and reported. For instance, Lv C. et al. explored $In(OH)_3$-S and demonstrated an outstanding Faradaic efficiency of 53.4% at -0.6 V vs RHE, with a urea production rate of 533.1 μg h^{-1} mg_{cat}^{-1} (Lv et al. 2021). In another study, Yuan M. et. al. introduced the concept of heterostructure formation and subsequently analysed their performance in simultaneous co-reduction of N_2 and CO_2 and reported Bi-$BiVO_4$ and $BiFeO_3$/$BiVO_4$ heterostructures, both operating at – 0.4 V vs RHE. The authors claimed that the former heterostructure achieved a production rate of 5.91 mmol h^{-1} g^{-1} with 12.55% Faradaic efficiency (Yuan et al. 2021a), while the latter showed

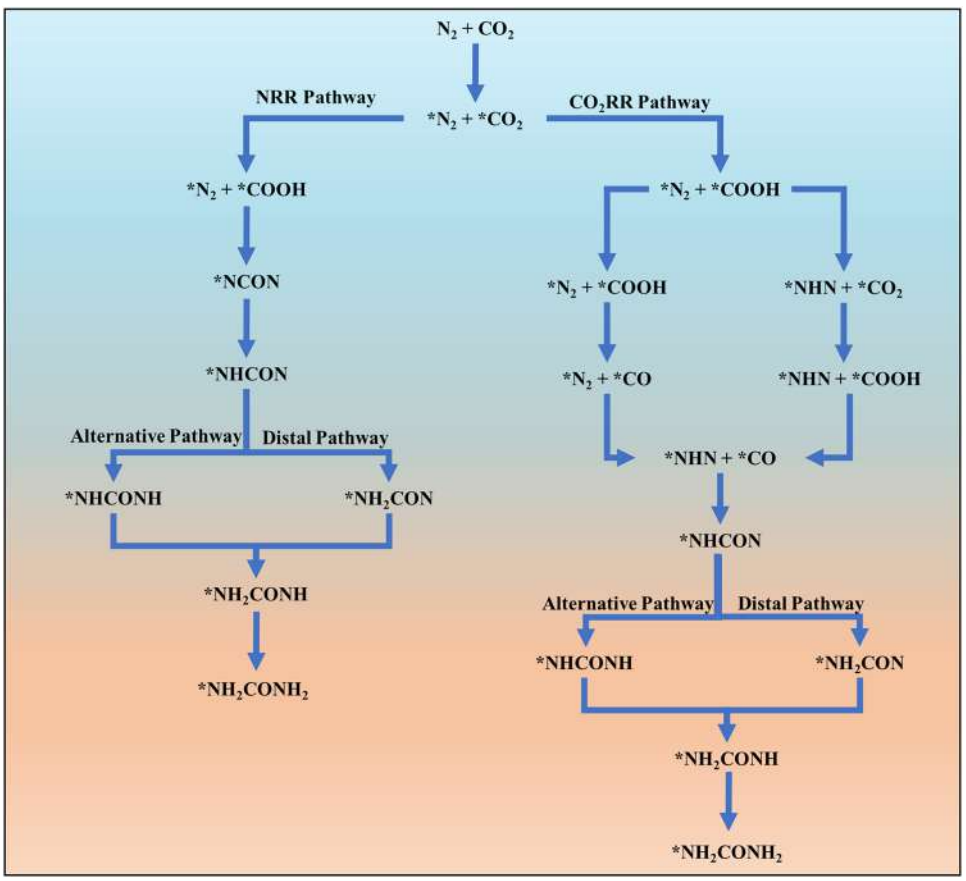

Fig. 2 Schematic illustrating the mechanistic pathway for electrochemical urea formation through simultaneous co-reduction of N_2 and CO_2 via both nitrogen reduction reaction pathway as well as carbon dioxide reduction reaction pathway for C-N coupling

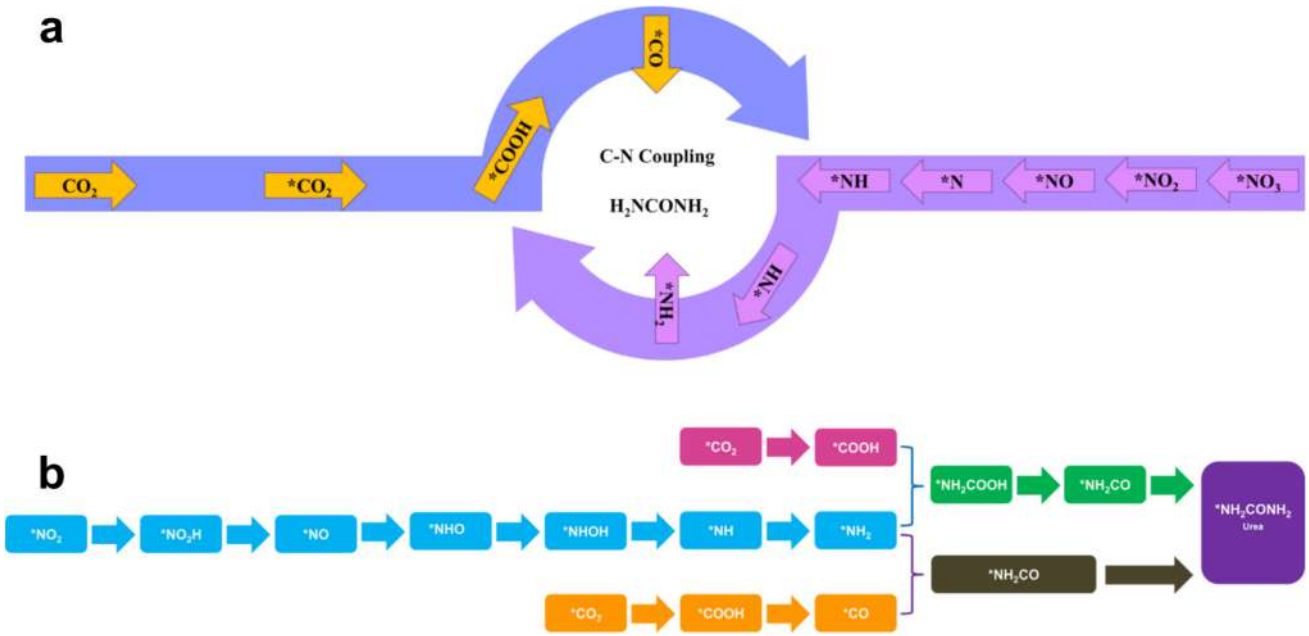

Fig. 3 **a** Mechanistic pathway for electrochemical reduction of nitrate and CO_2 for urea synthesis via C-N coupling **b** nitrite and CO_2 for urea synthesis via C-N coupling

a slightly lower production rate of 4.94 mmol h^{-1} g^{-1} but higher Faradaic efficiency at 17.18% (Yuan et al. 2021b). To the best of our knowledge, for the very first time, Huang Y. et. al. utilized nitric oxide as a nitrogen source for electrochemical urea synthesis. The research group fabricated Zn nanobelts electrochemically, and upon full studies, reported the urea production rate of 15.13 mmol g^{-1} h^{-1} along with a Faradaic efficiency of 11.26%, operating at -0.92 V vs. RHE (Huang et al. 2022).

The year 2022 brought further innovations, for instance, Wu W. et. al. for the very first time utilized bimetallic alloys and investigated the application of Cu-Bi alloy in urea electrosynthesis. The research group confirmed the source of both carbon and nitrogen from NMR studies and revealed the mechanism of urea synthesis on defective alloy by using in situ Raman spectroscopy (Wu et al. 2022). In another study, for the very first time Leverett J. et. al. studied and reported the use of single atom catalyst (SAC) the role of the Cu coordination structure in the simultaneous co reduction of CO_2 and NO_3^- where the Cu single atoms were confined in graphene sheets (Cu-GS-800). While achieving a Faradaic efficiency of 28% for urea production, the authors concluded the study with the confirmation that the Cu-N_4 sites possess higher selectivity for the CO_2RR, whereas both Cu-N_4 and Cu-N_{4-x}-C_x sites are more active toward the NO_3RR (Leverett et al. 2022). Later, Bharat G. et. al. prepared and studied Au nanosheets, and the prepared Au NSs photocathode demonstrated high stability over a period of 10 consecutive runs. A maximum urea yield rate of 98.5 μg_{urea} mg_{cat}^{-1} h^{-1} and FE of 22.7% at – 0.7 V vs. RHE was achieved while simultaneously co reducing N_2 and CO_2 for electrified urea production (Bharath et al. 2022). Liu X. et. al. explored carbon nanotubes with fluorine-rich as advanced metal-free electrocatalysts for urea synthesis. The group ended up getting a high yield rate of 6.36 mmol h^{-1} g_{cat}^{-1} for catalysed urea synthesis from NO_3^- with CO_2 using F-rich CNTs when compared with CNTs (Liu et al. 2022).

Interestingly, Mukherjee J. et al. explored the role of site selection while utilizing copper phthalocyanine nanotubes (CuPc NTs), which have multiple active sites (such as metal center, pyrrolic-N3, pyrrolic-N2, and pyridinic-N1). The researchers have exhibited a urea yield of 143.47 μg h^{-1} mg_{cat}^{-1} and faradaic efficiency of 12.99% at – 0.6 V RHE while reducing N_2 and CO_2 simultaneously. The group suggested while confirming from theoretical calculation, Pyridinic-N1 and Cu centers are responsible for forming CN bonds for urea by co-reduction of N_2 to NN* and CO_2 to *CO, respectively (Mukherjee et al. 2022b). While continuing their studies on electrochemical urea synthesis, Lv C. et al. explored defect-engineering and successfully synthesised electrocatalyst for high-efficiency urea synthesis under ambient conditions. The catalyst, consisting of indium oxyhydroxide with oxygen vacancy defects, achieved an excellent Faradaic efficiency of 51.0% at -0.5 V vs RHE (Lv et al. 2022). In another approach while exploring metal doping, Qin J. et al. synthesize another promising electrocatalyst that uses nitrate and carbon dioxide under ambient conditions over a Ru/Pt/

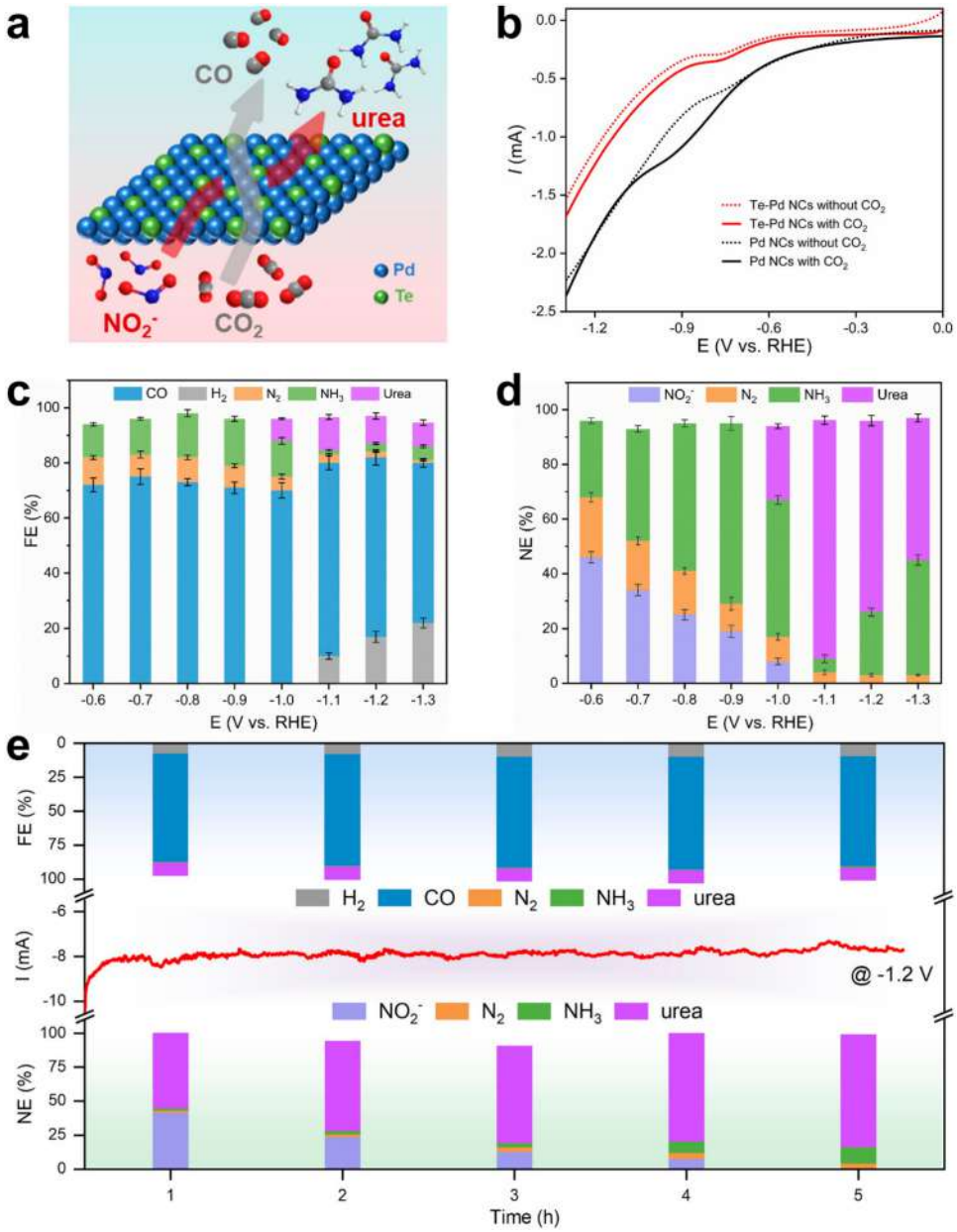

Fig. 4 **a** Schematic depicting electroreduction of CO_2 and NO_2^- using Te-Pd NCs/C for electrochemical urea synthesis. **b** LSVs for urea synthesis in 0.1 M $KHCO_3$ + 0.01 M KNO_2 solution in presence and absence of CO_2 saturated at a scan rate of 5 mV s^{-1} using Te-Pd NCs/C electrocatalyst **c** FE for various products obtained after electrochemical reduction **d** NE for N_2, $NO_3.^-$, NH_3 and urea at different applied potentials for urea production in CO_2-saturated 0.1 M $KHCO_3$ + 0.01 M KNO_2 solution on Te–Pd NCs/C. **e** Stability tests for continuous production of electrosynthesis of urea in 0.05 M KNO_2 electrolyte on Te–Pd NCs/C. "Reprinted (adapted) with permission from Nano Lett. 2020, 20, 11, 8282–8289. Copyright {2020} American Chemical Society"

Pd-modified three-dimensional copper foam electrode for urea synthesis. The Ru-Cu CF catalyst delivered a high urea yield of 151.6 μg h^{-1} cm^{-2} with a low onset potential and FE of 25.4%, surpassing that of Pt/Pd-Cu CF. While confirming from operando electrocatalytic Raman spectroscopy as well as theoretical calculations that the COOH intermediate formation is the rate determining step, the authors claimed that the Ru-Cu CF electrode also has the lowest formation energy of the COOH intermediate, which in turn accelerated the electrocatalytic urea synthesis (Qin et al. 2022).

Yuo et al. in 2023 developed a hybrid catalyst strategy to improve selectivity to urea by stabilizing key intermediates, $*CO_2NO_2$ and $*COOHNH_2$, using a relay catalysis mechanism. The as-synthesized Zn/Cu hybrid catalyst achieved an outstanding Faradaic efficiency of 75%, resulting in a urea production rate of 16 μmol h^{-1} cm^{-1}. This electrochemical urea production route claimed to reduces greenhouse gas emissions by 0.28 kg CO_2 per kg urea (Luo et al. 2023). Shin S. et. al. used the lithiation approach to create atomic-scale spacings (ds) between copper facets and prepared four samples with different ds values. The findings confirmed significant improvements in urea synthesis and concluded the research with achieving a remarkably high and outstanding urea yield rate of 7541.9 μg h^{-1} mg_{cat}^{-1} and a partial current density of 115.25 mA cm^{-2} with a d_s close to 6 Å with 51.9% Faradaic efficiency at -0.3 V vs RHE (Shin et al. 2023). Pan L. et al. explored single-atom $Pd_1 - TiO_2$ and dual atom $Pd_1Cu_1 - TiO_2$ for electrocatalytic

urea production. It was confirmed that the C-N coupling pathway and lower energy barrier of the dual-atom Pd_1Cu_1 site in $Pd_1Cu_1-TiO_2$ resulted in an ultrahigh urea activity of 166.67 $mol_{urea}\,mol_{Pd}^{-1}\,h^1$ with the corresponding 22.54% Faradaic efficiency at − 0.5 V vs RHE. Using a vacancy-anchorage approach, the researchers created two different kinds of catalysts: dual-atom $Pd_1Cu_1-TiO_2$ nanosheets and single-atom Pd_1-TiO_2 (Pan et al. 2023). Geng J. et. al. presented a liquid-phase laser irradiation method for fabricating graphitic carbon encapsulated iron and iron oxide nanoparticles on carbon nanotubes (Fe(a)@C-Fe_3O_4/CNTs). The nanoparticles show superior electrocatalytic activity for urea synthesis using NO_3^- and CO_2, achieving an high urea yield of 1341.3 ± 112.6 μg $h^{-1}\,mg_{cat}^{-1}$ and a faradic efficiency of 16.5 ± 6.1% at ambient conditions (Geng et al. 2023).

In one of the first studies of its kind, Zhang D. et al. reported a new catalyst system that can be used to synthesize industrial urea with high selectivity by growing graphdiyne in situ on the surface of cobalt–nickel mixed oxides that have a multi-heterojunction interfacial structure. By dramatically reducing by-product reactions that result in the generation of H_2, CO, N_2, and NH_3, the catalyst might efficiently maximize the intermediate's adsorption/desorption capabilities and encourage direct C–N coupling, according to mechanistic studies. With a record-high Faradaic efficiency of 64.3%, and urea yield rates of 913.2 μg $h^{-1}\,mg_{cat}^{-1}$, and exceptional long-term stability, the catalyst can directly synthesize urea from nitrite and carbon dioxide in water at room temperature and pressure at -0.7 V vs RHE (Zhang et al. 2023). In another insightful work, Wang Y et al. developed a Cu/ZnO-stacked tandem gas-diffusion electrode (GDE) for selective urea synthesis from electrocatalytic CO_2 and nitrate reduction reactions. The GDE, with an optimal ZnO/Cu CL area ratio, achieved a high Faradaic efficiency of 37.4% and a high yield of 3.2 μmol h^{-1} cm^{-2} for urea under ambient conditions, expanding the application of tandem electrodes and achieving cascade C–N coupling reactions (Wang et al. 2023).

Zhang Y et al. synthesised atomically dispersed Cu on In_2O_3 (Cu_1/In_2O_3) to co-electrolyse NO_3^- and CO_2 to achieve efficient and sustainable urea production. The authors confirmed the synergic effect of the Cu_1–O_2–In site and the Indium site to boost the energetics via a relay catalysis pathway, where the Cu_1–O_2–In site drives $*NO_3 \rightarrow *NH_2$ and the In site catalyses $*CO_2 \rightarrow *CO$ with the help of theoretical calculations and in situ spectroscopic analysis. In turn, the electrocatalyst resulted in an impressive urea yield rate of 28.97 mmol h^{-1} g^{-1} with a urea Faradaic efficiency (FE_{urea}) of 50.88% within a flow cell exhibits at -0.8 V vs RHE (Zhang et al. 2024). Li Y. et. al. in the very recent research while utilizing Cu_1/NC as an electrocatalyst for co-reduction of nitrogen wastes (NO_3^-) and CO_2, achieved an industrial scale high Faradaic efficiency of 62% as well as high urea yield rate of 596.1 μg mg^{-1} h^{-1} at -0.5 V vs RHE (Li et al. 2024b). Govindan B. et al. synthesized Ru–Pd alloyed nanoparticles and integrated them into 2D WO_3 and MXene nanosheets as part of an additional strategy to investigate bimetallic catalysts. With a faradaic efficiency of 23.7%, the Ru–Pd/WO_3/MXene electrocatalyst shows an impressive urea production of 227 μg_{urea} mg_{cat}^{-1} h^{-1} at -0.6 V vs RHE (Govindan et al. 2024). In order to study the effect of ligand introduction in phthalocyanine, Li H. et. al. explored the use of copper phthalocyanine (CuPc), from theoretical and experimental observation's it was confirmed that that the amino substitution results in strengthen and optimization of the electronic structure which results in an industry scale Faradaic efficiency of 67.4% along with a high rate of 103.1 ± 5.3 mmol h^{-1} g^{-1} (Li et al. 2024a). Cai H. et al. found that Fe-doped InOOH nanosheets effectively catalyse CO_2 and nitrate co-reduction, achieving a high Faradaic Efficiency of 26.9% and a yield rate of 980.6 μg h^{-1} mg_{cat}^{-1}. Theoretical calculations showed that iron dopants can tailor the reactivity of the Indium site, facilitating hydrogenation of the key CO_2NH_2 intermediate and suppressing hydrogen production with a higher energy barrier (Cai et al. 2024). Song X. et al. designed heterostructured Cu–Bi bimetallic catalyst for urea electrosynthesis, achieving a high urea Faradaic efficiency of 23.5% and a production rate of 2180.3 μg h^{-1} mg_{cat}^{-1} (Table 1).

The catalyst also demonstrated remarkable recycling stability. The introduction of moderate Bi induced the formation of a Bi–Cu/O–Bi/Cu_2O heterostructure with abundant phase boundaries, promoting *HONCON intermediate formation (Song et al. 2024). In the very recent developments led by Kaur et al electrodeposited bismuth (Bi) onto copper (Cu) foil, resulting in synthesis of Bi(0.01 V)@Cu,. The researchers demonstrated a high yield rate of 646 μg h^{-1} mg_{cat}^{-1} and an outstanding Faradaic efficiency of 70.7% V for urea production at − 0.45 V vs RHE. Additionally, the researchers employed various techniques such as isotopic labelling experiments, in situ electrochemical Raman spectroscopy, and the Fourier transform (FTIR) measurements, to understand the underlying urea formation mechanism (Kaur et al. 2024).

These developments highlight the rapid advancements in catalyst design for electrochemical urea synthesis, demonstrating improvements in both efficiency and production rates over the years. In some instances, the catalyst exceeded the industrial-scale limit for urea production rates, while in others, it achieved the industrial-scale Faradaic efficiency. However, no electrocatalyst has yet been explored or synthesized that surpasses both the industrial-scale yield rate and Faradaic efficiency requirements. There is a pressing need to investigate catalysts with multiple active sites capable of simultaneously reducing both

Table 1 Comparison of different electrocatalysts for electrochemical urea production

Catalyst	Potential V vs RHE	Source of nitrogen	Electrolyte	Urea production rate	Faradaic efficiency	Urea quantification methodology	References
Te-Pd NCs	− 1.1 V	NO_2^-	0.1 M $KHCO_3$	–	12.2%	Urease decomposition method	(Feng et al. 2020)
$In(OH)_3$-S	− 0.6 V	NO_3^-	0.1 M KNO_3	533.1 μg h^{-1} mg_{cat}^{-1}	53.4%	DAMO TSC	(Lv et al. 2021)
Bi-$BiVO_4$ heterostructures	− 0.4 V	N_2	0.1 M $KHCO_3$	5.91 mmol h^{-1} g^{-1}	12.55%	DAMO TSC	(Yuan et al. 2021a)
$BiFeO_3$/$BiVO_4$ Heterostructure	− 0.4 V	N_2	0.1 M $KHCO_3$	of 4.94 mmol h^{-1} g^{-1}	17.18%	DAMO TSC	(Yuan et al. 2021b)
Zn nanobelts	− 0.92 V	NO	0.2 M $KHCO_3$	15.13 mmol g^{-1} h^{-1}	11.26%	HPLC MS and 1 H NMR	(Huang et al. 2022)
InOOH nanoparticles	− 0.4 V		0.1 M $KHCO_3$	6.85 mmol h^1 g^1	20.97%	DAMO TSC	(Wu et al. 2022)
Cu SACs (Cu-GS-800)	− 0.9 V	NO_3	0.1 M $KHCO_3$ + 0.1 M KNO_3	4.3 nmol s^{-1} cm^{-2}	28%	DAMO TSC	(Leverett et al. 2022)
Au NSs photocathode	− 0.7 V	N_2	0.1 M $KHCO_3$	98.5 $\mu g_{urea} mg_{cat}^{-1}$ h^{-1}	22.7%	DAMO TSC	(Bharath et al. 2022)
F doped CNTs	− 0.65 V	NO_3^-	0.1 M KNO_3	6.36 mmol h^{-1} $g_{cat.}^{-1}$	18.0%	DAMO TSC	(Liu et al. 2022)
CuPc NTs	–0.6 V	N_2	0.1 M $KHCO_3$	143.47 μg h^{-1} mg^{-1}_{cat}	12.99%	DAMO TSC	(Mukherjee et al. 2022b)
V_O-InOOH	− 0.5 V	NO_3^-	0.1 M KNO_3	592.5 μg h^{-1} $mg_{cat.}^{-1}$	51.0%	DAMO TSC	(Lv et al. 2022)
The Ru-Cu CF	0.13 V	NO_3^-	0.1 M $NaNO_3$	151.6 μg h^{-1} cm^{-2}	25.4%,	DAMO TSC	(Qin et al. 2022)
Zn/Cu Hybrid catalysts	− 0.6	NO_3^-	0.1 M $KHCO_3$	16 μmol h^{-1} cm^{-2}	75%	NMR and DAMO TSC	(Luo et al. 2023)
Cu with facet modification	− 0.3 V	NO_3^-	1 M KOH + 0.1 M $KHCO_3$	7541.9 μg h^{-1} mg_{cat}^{-1}	51.9	1H NMR	(Shin et al. 2023)
Pd_1Cu_1 − TiO_2	− 0.5	N_2	0.1 M $KHCO_3$	166.67 mol_{urea} mol_{Pd}^{-1} h^1	22.54%	DAMO TSC	(Pan et al. 2023)
Fe(a)@C-Fe_3O_4/CNTs	− 0.65 V	NO_3^-	0.1 M KNO_3	1341.3 ± 112.6 μg h^{-1} mg_{cat}^-	16.5 ± 6.1%	DAMO TSC	(Geng et al. 2023)
Co–NiO_x@GDY	− 0.7 V	NO_2^-	0.01 M $NaNO_2$	913.2 μg h^{-1} mg_{cat}^{-1}	64.3%,	DAMO TSC	(Zhang et al. 2023)
ZnO/Cu CL	− 0.3 V	NO_3^-	0.1 M KNO_3	3.2 μmol h^{-1} cm^{-2}	37.4%	DAMO TSC	(Wang et al. 2023)
Cu on In_2O_3 (Cu_1/In_2O_3)	− 0.8 V	NO_3^-	0.1 M KNO_3 and 0.1 M $KHCO_3$	28.97 mmol h^{-1} g^{-1}	50.88%	Urease decomposition method	(Zhang et al. 2024)
Cu_1/NC	− 0.5 V	NO_3^-	0.1 M $KHCO_3$ + 0.1 M KNO_3	596.1 μg mg^{-1} h^{-1}	62%	DAMO TSC	(Li et al. 2024b)
Ru–Pd/WO_3/MXene	− 0.6 V	N_2	0.5 M $NaNO_3$ + 0.5 M $NaHCO_3$	227 μg_{urea} mg_{cat}^{-1} h^{-1}	23.7%	DAMO TSC	(Govindan et al. 2024)
CuPc-Amino	− 1.6 V	NO_3^-	0.1 M $KHCO_3$ and 0.05 M KNO_3	103.1 ± 5.3 mmol h^{-1} g^{-1}	11.9 ± 0.6%	Urease decomposition method	(Li et al. 2024a)
Fe-doped InOOH nanosheets	− 0.8 V	NO_3^-	0.1 M $KHCO_3$ + 0.1MKNO_3	980.6 μg h^{-1} $mg_{cat.}^{-1}$	26.9%	Urease decomposition method	(Cai et al. 2024)
Cu–Bi bimetallic catalysts	− 0.6 V	NO_3^-	0.2 M $KHCO_3$ + 0.1 M KNO_3	2180.3 μg h^{-1} mg_{cat}^{-1}	23.5%	Urease decomposition method and ^{1}H NMR	(Song et al. 2024)

Table 1 (continued)

Catalyst	Potential V vs RHE	Source of nitrogen	Electrolyte	Urea production rate	Faradaic efficiency	Urea quantification methodology	References
Bi(0.01 V)@ Cu	− 0.45 V	N_2	0.1 M $KHCO_3$	646 μg h^{-1} mg_{cat}^{-1}	70.7%	DAMO TSC	(Kaur et al. 2024)

CO_2 and nitrogen sources while maintaining stability over an extended period.

Challenges and future prospects

Electrochemical urea synthesis through C-N coupling encounters significant challenges due to the inert nature of CO_2 and nitrogenous molecules (N_2, NO_3^-), as well as the prevalence of competing side reactions. The mismatched orbital symmetry between CO_2 and N_2 intermediates impedes electron transfer, rendering the coupling process energetically demanding. Additionally, the reduction kinetics of CO_2 and nitrogen species are often incompatible, resulting in inefficient co-reduction and low urea yield rates. Stabilizing key intermediates such as *CO and $*NO_2$ is crucial for enhancing coupling efficiency; for instance, $CuWO_4$ bimetallic catalysts have demonstrated promise by lowering energy barriers and increasing urea production rates. Furthermore, designing catalysts with adjacent dual sites (e.g., Pd-Cu alloys) or bonded diatomic pairs (e.g., Fe–Ni) can facilitate the coordination, adsorption, and activation of reactants, thereby overcoming kinetic barriers and improving C-N coupling efficiency. Despite advancements in catalyst design and mechanistic understanding, achieving high efficiency under mild conditions remains a challenge that necessitates further optimization of active sites, stabilization of intermediates, and suppression of side reactions.

"Mitigating by-product challenges in electrocatalytic C–N coupling: strategies for selective CO_2 reduction and N_2 activation in urea synthesis"

Electrochemical urea synthesis through the C-N coupling reaction using CO_2 and N_2 represents a promising green approach to sustainable nitrogen fixation. However, various competing reactions and by-products can impede this process. A comprehensive understanding of these competing pathways, along with strategies to mitigate their effects, is essential for achieving high selectivity and efficiency in urea production.

One of the primary obstacles is the hydrogen evolution reaction (HER), which competes for electrons and protons, thereby reducing the efficiency of CO_2 and N_2 reduction. This issue is further exacerbated in aqueous systems, where water is readily reduced to hydrogen gas, diverting resources from the desired C-N coupling process. Additionally, the formation of carbon monoxide (CO) and methane (CH_4) presents substantial challenges, as CO_2 reduction can yield CO instead of carbamate intermediates, while CH_4 formation results in the loss of valuable carbon reactants. CO, in particular, is problematic because it strongly binds to catalyst surfaces, poisoning active sites and impeding effective N_2 activation. Similarly, ammonia (NH_3) formation competes directly with C-N bond formation, as many electrocatalysts, especially transition metals like iron (Fe) and molybdenum (Mo), tend to favor the reduction of N_2 to NH_3 over urea synthesis(Guo et al. 2024). The formation of carbonate (CO_3^{2-}) and formate ($HCOO^-$) negatively impacts the process, as CO_2 in alkaline electrolytes tends to react with hydroxide ions, thereby reducing the availability of CO_2 for catalysis and shifting the equilibrium away from productive C-N coupling. Additionally, the formation of NO_3^- and NO_2^- from the partial oxidation of N_2 can lead to nitrogen loss, further diminishing the efficiency of the process. To address these challenges, researchers are investigating advanced catalyst engineering strategies, including bimetallic and single-atom catalysts that provide distinct active sites for CO_2 and N_2 activation, as well as defect engineering techniques to enhance selectivity. Optimizing electrolytes with ionic liquids and controlled pH environments can help suppress competing side reactions. Furthermore, adjustments to reaction conditions, such as precise potential control and the use of gas-diffusion electrodes, can improve efficiency by maintaining high local concentrations of CO_2 and N_2. By integrating these strategies, it is possible to minimize side reactions and enhance the selectivity and efficiency of electrocatalytic urea synthesis, making it a viable alternative for sustainable nitrogen fixation.

Challenges in detection of electrochemically synthesised urea

The detection and quantification of urea in electrochemical urea synthesis are crucial for evaluating the efficiency and

performance of the process. Several methods, including the diacetyl monoxime method, nuclear magnetic resonance (NMR) spectroscopy, urease decomposition method, and high-performance liquid chromatography (HPLC) coupled with mass spectroscopy, have been developed for the detection and quantification of urea in various samples, each with its own advantages and limitations(Kohlhaas et al. 2024).

1. The diacetyl monoxime—Thiosemicarbazide (DAMO-TSC) method: The method relies on the formation of a colored complex between urea and diacetyl monoxime in an acidic environment containing ferric chloride and thiosemicarbazide. This reaction produces a red complex that can be quantified spectrophotometrically by measuring absorbance at 525 nm. While this method is relatively straightforward and can detect low concentrations of urea, it has its own set of limitations.
2. Nuclear magnetic resonance (NMR): NMR spectroscopy provides a more precise method for urea quantification that is less affected by interfering substances. The ^{1}H NMR technique detects urea based on the unique chemical shift of its hydrogen atoms. The primary advantage of the NMR method lies in its specificity; it is generally influenced by electrolyte ions, by-products or metal ions that might interfere with other detection methods. However, this technique requires specialized equipment and can be more time-consuming than colorimetric methods.
3. The urease method is a common technique used for urea detection, which involves the enzymatic breakdown of urea into CO_2 and NH_3. Nitrite ions can inhibit the formation of the indophenol derivative, leading to underestimation of ammonia production. High levels of ammonia can result in background increases that may cause overestimation. Additionally, certain metal ions such as cobalt (Co^{2+}), iron (Fe^{3+}), and manganese (Mn^{2+}) can inhibit urease activity, leading to lower measured concentrations of urea.
4. High-performance liquid chromatography (HPLC) offers another robust method for determining urea levels. It separates components based on their interactions with a stationary phase as they pass through a mobile phase. HPLC requires specialized equipment and may involve more time-consuming procedures compared to simpler colorimetric methods.

Limitations of DAMO TSC method

The DAMO-TSC method is a widely utilized colorimetric technique for the electrochemical detection of urea; however, it has several significant limitations that impact its accuracy, sensitivity, and applicability in real-world electrochemical systems. One of the primary drawbacks is interference from other nitrogen-containing species, such as NH_3, NO_3^-, and NO_2^-, which can react with the DAMO-TSC reagent, resulting in false-positive outcomes and an overestimation of urea concentration. Furthermore, the method necessitates strict pH control to ensure consistent colour development, as variations in pH can alter the reaction kinetics and affect the intensity of the measured absorbance. Another limitation is the low selectivity for urea in complex electrolyte environments, particularly in electrochemical systems where multiple reaction by-products are present. Additionally, the method has a limited detection range and sensitivity, rendering it unsuitable for detecting ultra-low concentrations of urea, which is critical in applications such as electrocatalytic urea synthesis. Furthermore, the colorimetric reaction is time-dependent, meaning that prolonged exposure to the reagent can lead to deviations in absorbance readings, thereby diminishing reproducibility and reliability. The DAMO-TSC method also employs toxic organic reagents, which raise environmental and handling concerns, limiting its suitability for large-scale or in-situ monitoring applications. Additionally, the dependence on spectrophotometry for quantitative analysis may impede its integration with real-time electrochemical monitoring systems. To address these limitations, alternative detection methods, such as HPLC, NMR and urease method are being explored for more selective, sensitive, and interference-free urea detection in electrochemical systems.

Recently explored and careful studies conducted by Chen et al. resulted in modification of the existing traditional DAMO-TSC method for urea detection [40]. It has been identified that the NO_2^- presence significantly affects and changes the detection limit as well as the accuracy of urea concentration and hence a simple nitrite elimination method has been reported which confirmed the accurate urea identification as depicted in Fig. 5. To ensure reliable urea detection in electrochemical synthesis processes, researchers should take several measures, including using isotope labelling techniques to confirm both production and quantification accurately, developing standard curves for each detection method using known concentrations of urea, implementing proper controls and blanks to account for background signals or matrix effects, and regular calibration of instruments and validation of methods. By carefully selecting and optimizing urea detection methods while considering potential interferences and methodological limitations, researchers can significantly enhance the accuracy and reliability of urea quantification in electrochemical synthesis processes.

Strategies and future prospects for electrochemical urea synthesis

Strategies for improving C-N coupling in electrochemical urea synthesis are crucial for enhancing both efficiency and sustainability. One approach involves doping established catalysts to optimize their electronic properties, which facilitates better adsorption and activation of reactants such as CO_2 and nitrogenous species like nitrogen/nitrate/nitrites. For instance, introducing bonded iron-nickel (Fe–Ni) pairs as diatomic catalysts enhance synergistic interactions between active sites, promoting thermodynamically favorable and kinetically efficient C-N coupling. To lower the energy barriers for bond formation, another tactic focuses on improving existing active sites by adjusting their atomic configurations to stabilize intermediates such as *CO and *NH. Additionally, incorporating oxyphilic surface sites can enhance selectivity and reduce competing side reactions, such as hydrogen evolution, by favouring the binding of intermediates containing oxygen. To encourage the formation of C-N bonds, catalysts are designed to selectively accept electrons from reactants and subsequently return them. This process is known as electron acceptance and back-donation. Additionally, dual active sites or heterojunctions are added to stabilize the carbon and nitrogen intermediates at the same time, guaranteeing matching kinetics of the NO_3^- reduction events and the CO_2 reduction reactions for effective coupling. Together, these tactics seek to address issues including limited selectivity, competing reactions, and high energy barriers in order to enable green urea production in ambient circumstances. Therefore, it can be concluded that strategies such as the introduction of vacancies, defect engineering, the formation of heterojunctions, the exploration of bimetallic or trimetallic active sites, and the utilization of single-atom catalysts, along with the optimization of reaction conditions (e.g., flow rate, concentration, pH, and potential), should be systematically investigated to improve the efficiency of electrochemical urea synthesis.

Establishing the mechanism for electrochemical urea synthesis: the role of in-situ and ex-situ techniques

A number of groups across the globe has been utilizing different in-situ as well as ex situ techniques to fully understand the underlying mechanism for urea mechanism. In situ techniques such as in situ Raman spectroscopy, Fourier transform infrared (FTIR), differential electrochemical mass spectrometry (DEMS) etc. have been utilized to identify the intermediates as well as their corresponding peaks, which are generated during electrochemical urea production

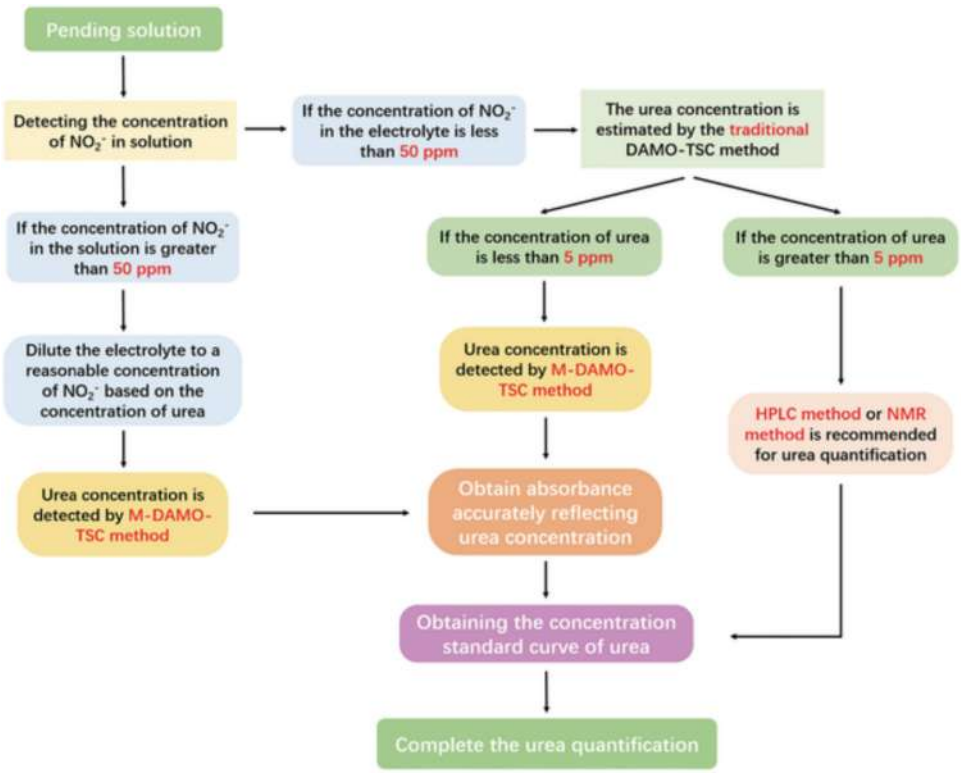

Fig. 5 Proposed revised approach for the quantification of electrochemically synthesized urea utilizing the M-DAMO-TSC technique (Chen et al. 2023) (reproduced with permission)

during the course of electrochemical co reduction of N_2 and CO_2 (Wu et al. 2022; Kaur et al. 2024; Zhang et al. 2024) Therefore, it can be concluded that, there is a need to focus on synthesis of catalysts with multiple active sites which can be utilized simultaneously to activate both nitrogen as well as CO_2 and the catalyst should be studied thoroughly with the help of in-situ as well as ex-situ techniques to understand the underlying mechanism for urea production via electrocatalysis. As of now, the need of the hour is to develop and utilize more and more cost effective in-situ as well as ex-situ techniques which can be easily utilized to confirm the intermediates which in turn help establishing the exact reaction mechanism being followed by the electrocatalyst for urea production.

Conclusion

The exploration of electrochemical urea synthesis is still in its infancy, and the primary focus of current research is on new materials and catalysts. Thus, this study concludes by discussing current advancements in catalyst design and research methods as well as new materials that expedite the processes of urea synthesis. We emphasize the importance for enhancing reaction conditions and integrating renewable energy sources in years to come to further develop this technology. To make the reduction of nitrogen species to urea production easier, some obstacles must be surmounted. It is in particular complicated to co-reduce two different substrates in multiple steps to produce a single output. Effective and selective catalysts are vital in minimizing the production of multiple byproducts and ensuring stable operation in mild environments. Additionally, it is critical to build electrochemical cells that optimize the gaseous and liquid conveyance of the reactant for this co-reduction while enabling a sufficiently high yield, energy efficiency, and scalability. However, a thorough understanding of the entire electrochemical cell process is crucial for the swift successful development of electrochemical urea production in order to avoid challenges. In order to address the challenges in the field of C-N coupling for the electrosynthesis of urea, this thorough review gathers the latest advancements made, particularly in the last five years. This, in turn, provides guidance for the development of advanced C-N coupling frameworks with improved urea synthesis.

Data availability All data analyzed during this study are included in this published article.

Declarations

Competing interests The authors declare no competing interests.

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