

Review

# Carbon Dioxide and Nitrate Electrocatalytic C-N Coupling for Sustainable Production of Urea

Litao Jia and Fanghua Li \*

School of Environment, Harbin Institute of Technology, Harbin 150090, China

\* Correspondence: fanghuahe01@hit.edu.cn

Received: 15 December 2023; Revised: 17 January 2024; Accepted: 19 February 2024; Published: 5 March 2024

**Abstract:** The electrocatalytic co-reduction of carbon dioxide ( $\text{CO}_2$ ) and nitrate ( $\text{NO}_3^-$ ) for urea synthesis under environmental conditions offers a promising solution for achieving sustainable environmental management. Besides, electrochemical urea synthesis is an alternative approach for cleaner production of urea compared to the conventional urea industrial production process with high energy consumption and pollution. However, lower urea yield, lower selectivity and unclear C-N coupling reaction mechanism are still the main challenges to its large-scale application. In this review, we focus on accurate and reliable detection methods and evaluation criteria for urea products, recent progress on  $\text{CO}_2$  and  $\text{NO}_3^-$  electrocatalytic co-reduction synthesis of urea, rational design of high-performance electrocatalysts, and C-N coupling reaction mechanism of urea electrochemical synthesis under atmospheric conditions. This review could contribute to the development of electrochemical urea synthesis via effective remediation of  $\text{CO}_2$  and  $\text{NO}_3^-$ .

**Keywords:** urea synthesis; C-N coupled system; electrocatalytic co-reduction; reaction mechanism; multiphase electrocatalysts

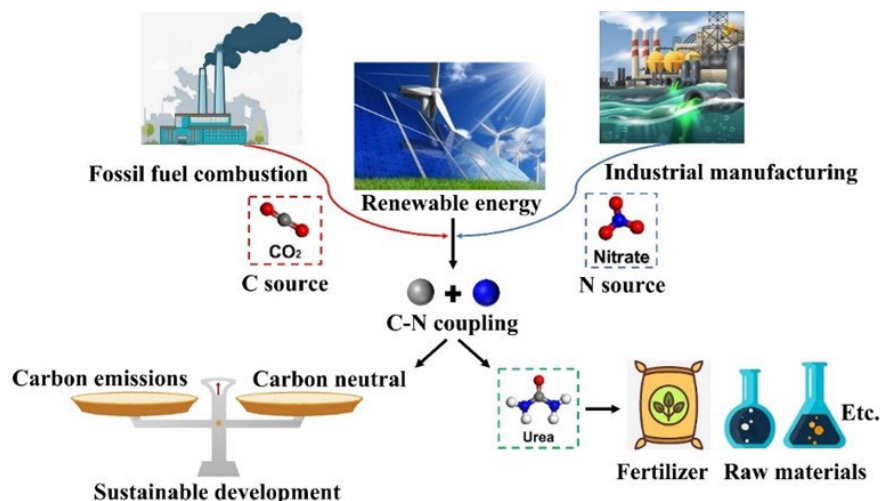
## 1. Introduction

Carbon Capture and Utilization (CCU) is a promising solution for converting  $\text{CO}_2$  into valuable chemical products, reducing the greenhouse effect caused by its emission into the atmosphere, and achieving “carbon peaking and carbon neutrality” [1,2]. Not only may CCU be used with C/H/O-based reactants, but it can also be used to synthesize useful compounds other than simple carbon species [3,4]. For example, the addition of nitrogen can form C-N bonds and generate organic nitrogen compounds [5]. These products have a variety of chemical and biological activities, are very important chemical intermediates or raw materials, have broad application prospects and market value is therefore very important [6]. Of particular importance is the production of urea using the electrocatalytic co-reduction C-N coupling of naturally occurring molecules and environmental pollutants, such as  $\text{CO}_2$  and  $\text{NO}_3^-$ , as sources of C and N [7,8] (Figure 1).

Compared with the traditional energy-intensive process for urea synthesis, this approach reduces the dependence on fossil fuels and  $\text{CO}_2$  emissions, which not only enables the effective use of  $\text{CO}_2$  but also helps to control water pollution and ultimately achieve the efficient green synthesis of urea, which is of high significance for climate change mitigation and environmental protection [9]. However, this attractive approach is still in its infancy, yields and selectivity of the target product are still low, and it faces many problems in terms of economic efficiency, so there is still a long way to go to achieve industrialization [10,11]. The logical design of electrocatalysts, the benefits of utilizing nitrate as an N source, the reaction mechanism of C-N coupling, and precise and dependable detection techniques for the products of electrocatalytic urea production have also received little attention in reviews [12].

This review includes an overview of the developments in the field of electrochemical urea synthesis research, the rational design of high-performance electrocatalysts, the reaction mechanism of C-N coupling in the electrochemical urea synthesis under ambient conditions, and the more precise and reliable detection of lower urea yields. We also provide an overview of the primary challenges facing multiphase electrocatalytic urea production. This work also aims to stimulate future research towards the overall enhancement of C-N coupling system performance and product efficiency, by looking ahead to the research direction and development opportunities in this sector. The advancement of electrochemical urea production in industry is aided by this review.





**Figure 1.** Cleaner production of urea from the catalytic coupling of CO<sub>2</sub> and nitrate.

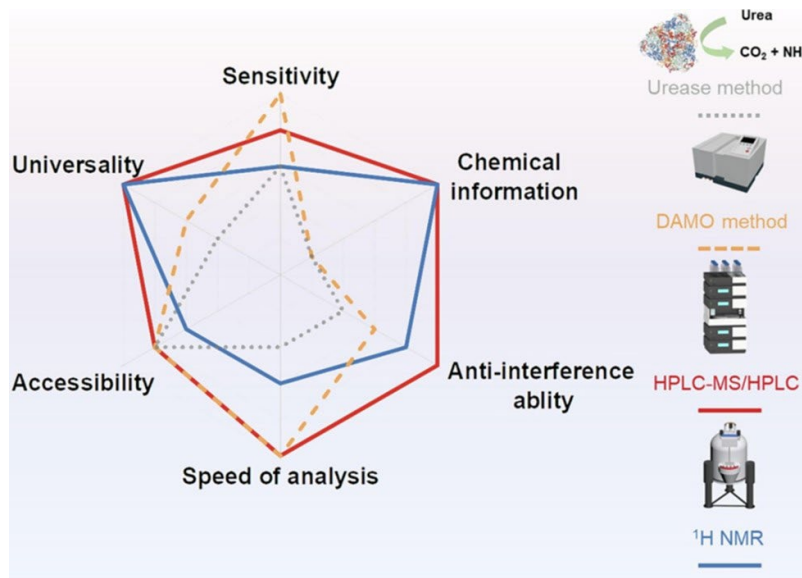
## 2. Advances in Electrocatalytic C-N Coupling Research

### 2.1. Urea Product Detect Techniques and Reliable Quantification

The electrocatalytic co-reduction C-N coupling of CO<sub>2</sub> and NO<sub>3</sub><sup>-</sup> to synthesize urea is not only a promising strategy for carbon neutrality and wastewater treatment, but also a promising approach for energy-saving and sustainable urea synthesis. However, the performance of the current electrocatalyst shows low activity. The reaction system needs to be optimized while the reaction mechanism is still unclear, resulting in a low yield and selectivity of urea. Therefore, such low concentrations of urea are very susceptible to interference during the test [13]. To evaluate the quality of urea more accurately, urea detection methods and the advantages and disadvantages of each method have been reviewed, to provide guidance for researchers to choose the appropriate urea detection method. The main testing methods for urea products are the urease decomposition method, diacetyl monoxime method (DAMO), high-performance liquid chromatography (HPLC), and <sup>1</sup>H nuclear magnetic resonance (<sup>1</sup>H NMR) [5,13–15]. In addition, possible interferents (liquid byproducts or dissolved metal ions) generated during urea synthesis have an impact on the quantification of urea detection when the urea concentration is at the nmol/μmol level.

Specifically, NO<sub>2</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> had a significant interfering effect on urea quantification, and the presence of ions such as Co<sup>2+</sup>, Fe<sup>2+</sup> and Mn<sup>2+</sup> also led to inaccurate detection of urea concentrations [13,16]. Furthermore, differences in urease activity produced by different batches, possible NH<sub>4</sub><sup>+</sup> loss during heating, and the inhibition of NH<sub>4</sub><sup>+</sup> determination by colorimetric methods by high urease concentrations may have an impact on the quantitative urea test.

Reducing substances such as NO<sub>2</sub><sup>-</sup> and S<sub>2</sub>O<sub>3</sub><sup>2-</sup>, thiourea, thiosulfate, etc. can also interfere with the accuracy of urea quantification when determining urea content by the DAMO method [17,18]. The <sup>1</sup>H NMR method's detection limit for urea testing is 0.42 ppm. Temperature, pH, and solvent all affect the signal intensity of active hydrogen, which can distort test findings. One benefit of using <sup>1</sup>H NMR for quantifying urea is that the presence of metal ions or byproducts does not have a substantial impact on the measurement of urea since each compound's hydrogen atoms have a distinct chemical coordination environment [13]. When testing urea concentration by HPLC, a 5 μm NH<sub>2</sub> column is usually used, with acetonitrile-water as the mobile phase [19]. This method has the advantages of high resolution, good reproducibility, and less interference from impurities. The presence of CO<sub>2</sub> reduction intermediates such as HCOO<sup>-</sup>, CH<sub>3</sub>OH and CH<sub>3</sub>CH<sub>2</sub>OH, NO<sub>3</sub><sup>-</sup> reduction by-products NH<sub>4</sub><sup>+</sup> and NO<sub>2</sub><sup>-</sup>, and C-N coupling by-products (e.g., formamide and acetamide) does not significantly interfere with the accurate quantification of urea by HPLC [20,21]. The sensitivity, versatility, ease of use, chemical information, speed of analysis and immunity to interference of the assays were objectively assessed and compared based on a thorough examination of the different assays mentioned above, as shown in Figure 2. The single urea quantification methods all have drawbacks and are difficult to quantify accurately for trace amounts of urea. Therefore, synergistic methods may be the development trend to retain the advantages of detection to overcome the defects of detection and to achieve accurate quantification. Fortunately, high-performance liquid chromatography-mass spectrometry (HPLC-MS) can avoid these problems and is considered a more suitable method for urea quantification at this stage.



**Figure 2.** Comparison of four common urea testing methods [22].

## 2.2. The Progress of Electrocatalytic Co-Reduction of Carbon Dioxide and Nitrate for Urea Synthesis

Electrochemical urea synthesis has shown promising potential in the field of energy and environmental sustainability. Previous studies have focused on the development of  $\text{CO}_2$  and different nitrogen-containing species (e.g.,  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ ,  $\text{NH}_3$ ,  $\text{N}_2$  and  $\text{NO}$ ) for urea synthesis.

In previous reports of electrocatalytic synthesis of urea, the most studied N sources are  $\text{NH}_3$  and  $\text{N}_2$ . However, there are disadvantages to using  $\text{NH}_3$  and  $\text{N}_2$  as N sources [23]. Additional processes such as  $\text{NH}_3$  collection and air separation of  $\text{N}_2$  elevate the cost and show lower Faraday efficiency (FE) [24]. There are several benefits to using  $\text{NO}_3^-$  as a source of N. First,  $\text{NO}_3^-$  is widely distributed in the natural world, particularly in industrial wastewater. Unlike other N sources, which require additional processes and energy consumption to obtain,  $\text{NO}_3^-$  is readily available as an environmental waste [25]. Secondly, the maximum concentration of  $\text{NO}_3^-$  in drinking water should be limited to less than 10 mg/L because excessive  $\text{NO}_3^-$  ingestion may cause disease. Therefore, using  $\text{NO}_3^-$  as an N source can achieve high-value conversion of environmental pollutants, solving the environmental problems caused by  $\text{NO}_3^-$  and converting waste into valuable chemicals, which is extremely beneficial to environmental sustainability [26,27]. In addition to this, the chemical stability of  $\text{N}_2$  and the low solubility of  $\text{N}_2$  in the electrolyte require a large amount of energy to activate the reactants and carry out the coupling reaction [28]. In this respect, the N=O bond dissociation energy of  $\text{NO}_3^-$  ( $204 \text{ kJ mol}^{-1}$ ), contrasts with that of the N≡N bond ( $941 \text{ kJ mol}^{-1}$ ) [29,30]. Therefore, electrochemical reduction of  $\text{CO}_2$  and  $\text{NO}_3^-$  to synthesize urea offers a promising and feasible solution for pollution and carbon reduction.

Researchers have made outstanding contributions to the investigation of electrocatalytic  $\text{CO}_2$  and nitrate co-reduction to urea. However, the low yield and selectivity of urea remain the most important problems to be solved in this direction (Table 1). Electrocatalytic co-reduction systems need to achieve current densities of hundreds of  $\text{mA/cm}^2$  and >50% selectivity of the target product to be economically viable for the electrosynthesis of urea [7,31,32]. Consequently, the design and preparation of superior electrocatalysts is an important measure to improve the yield and selectivity of urea electrosynthesis. This review focuses on the recent studies and electrocatalysts (precious metal catalysts, transition metal catalysts, single-atom catalysts, carbon-based catalysts and surface defects) used for electrocatalytic  $\text{CO}_2$  and  $\text{NO}_3^-$  synthesis of urea under ambient conditions, providing some references for the design and preparation of high-performance electrocatalysts.

**Table 1.** Comparison of recently reported work on the synthesis of urea by electrocatalytic  $\text{CO}_2$  and  $\text{NO}_3^-$  co-reduction.

Electrocatalyst	Urea Yield	FE <sub>Urea</sub> (%)	Reference
Fe(a)@C-Fe <sub>3</sub> O <sub>4</sub> /CNTs	1341.3 ± 112.6 $\mu\text{g h}^{-1} \text{mg}_{\text{cat}}^{-1}$	16.5 ± 6.1	[33]
CoPc-COF@TiO <sub>2</sub> NTs	1205 $\mu\text{g h}^{-1} \text{cm}^{-2}$	49	[34]
F-CNTs	6.36 $\text{mmol h}^{-1} \text{g}_{\text{cat}}^{-1}$	18	[35]
Cu <sub>2</sub> O (ds)	7541.9 $\mu\text{g h}^{-1} \text{mg}_{\text{cat}}^{-1}$	51.97 ± 0.8	[36]
MoO <sub>x</sub> /C	1431.5 $\mu\text{g h}^{-1} \text{mg}_{\text{cat}}^{-1}$	27.7	[37]

Ru-Cu CF	151.6 $\mu\text{g h}^{-1} \text{cm}^{-2}$	25.4	[38]
Core-shell Cu@Zn	7.29 $\mu\text{mol cm}^{-2} \text{h}^{-1}$	9.28	[39]
Cu <sub>1</sub> -CeO <sub>2</sub>	52.84 $\text{mmol h}^{-1} \text{g}_{\text{cat}}^{-1}$	-	[40]
Fe-Ni-DASC	20.2 $\text{mmol g}^{-1} \text{h}^{-1}$	17.8	[41]
In (OH) <sub>3</sub> -S	533.1 $\mu\text{g h}^{-1} \text{mg}_{\text{cat}}^{-1}$	53.4	[9]
Cu-N-C	-	28	[42]
AuPd	204.2 $\mu\text{g mg}^{-1} \text{h}^{-1}$	15.6	[21]
V <sub>o</sub> -InOOH	592.5 $\mu\text{g h}^{-1} \text{mg}_{\text{cat}}^{-1}$	51	[18]

### 2.2.1. Precious Metal Catalysts

In addition to being crucial for electrocatalysis, precious metals and alloys have demonstrated exceptional performance in the co-reduction of CO<sub>2</sub> and NO<sub>3</sub><sup>-</sup> to produce urea by electrocatalysis. To synthesize carbon dioxide-coupled NO<sub>3</sub><sup>-</sup> to urea in a highly selective and active manner, Qin et al. [38] developed an electrode via in-situ deposition that was anchored to a three-dimensional copper foam (Ru/Pt/Pd-Cu CF). Remarkably high yield and selectivity (urea yield of 151.6  $\mu\text{g h}^{-1} \text{cm}^{-2}$  and FE of 25.4%) were obtained at a low potential of -0.3 V vs. Ag/AgCl using the noble metal alloy catalyst. The reason for this excellent performance is that the presence of Ru in the Ru/Pt/Pd-Cu CF facilitates the generation of \*NH<sub>2</sub> and provides strong adsorption energy for the stabilization of the \*COOH intermediate [38]. Wang et al. [21] synthesized AuPd nanoalloy electrocatalysts for the simultaneous reduction of CO<sub>2</sub> and NO<sub>3</sub><sup>-</sup> under ambient conditions. Besides, the synthesized catalysts showed excellent catalytic performance with urea production rates up to 204.2  $\mu\text{g mg}^{-1} \text{h}^{-1}$  and FE of 15.6%. Although precious metals have excellent performance, their expensive price limits their wide application. The preparation of alloys of precious metals with other inexpensive metals is one of the promising methods for utilizing precious metals. This is because the excellent catalytic properties of precious metals can be retained and the amounts of precious metals used can be reduced.

### 2.2.2. Transition Metal Catalysts

Transition metals are widely studied in the field of electrocatalysis due to their unique outer electronic structure [43,44]. With an optimized urea yield rate and FE over Cu@Zn [39], the self-supported core-shell Cu@Zn nanowires demonstrated excellent performance in urea electrosynthesis, reaching 7.29  $\mu\text{mol cm}^{-2} \text{h}^{-1}$  and 9.28% at -1.02 V vs RHE, respectively. According to research by Seokmin et al. [36], copper (Cu) with atomic-scale spacing (ds) between copper facets can greatly increase the electrochemical urea synthesis efficiency of CO<sub>2</sub> and NO<sub>3</sub><sup>-</sup>. By varying the degree of lithiation on each sample, they were able to create ds between the Cu faces in four different Cu samples with varying ds values. Out of the four samples, Cu with ds close to 6 Å exhibited superior electrocatalytic performance (Figure 3d-f), yielding 7541.9  $\mu\text{g h}^{-1} \text{mg}_{\text{cat}}^{-1}$  and 115.25  $\text{mA cm}^{-2}$  at 0.41 V<sub>RHE</sub> for urea. The urea yield of this compound is 444.7  $\mu\text{g h}^{-1} \text{mg}_{\text{cat}}^{-1}$  and its partial current density is 1.96  $\text{mA cm}^{-2}$ , which is significantly higher than bare Cu, and also has a stability of up to 50 h [36]. Transition metals are the most promising alternative to precious metal catalysts. Thus, the design and preparation of excellent transition metal catalysts has a highly broad development prospect. The design of superior transition metal catalysts should emphasize the active site of the catalyst, the modulation of the electronic structure, and the adsorption-desorption with the reactants. A strategy to improve urea selectivity using a hybrid catalyst (Zn/Cu) is reported by Luo et al. [45]. The catalytically active sites of the two transition metals were able to independently stabilize the key intermediates \*CO<sub>2</sub>NO<sub>2</sub> and \*COOHNH<sub>2</sub> required for urea formation through a relay catalytic mechanism. At 1,000 parts per million of NO<sub>3</sub><sup>-</sup> in wastewater, the catalyst demonstrated a 75% FE, while producing 16  $\mu\text{mol h}^{-1} \text{cm}^{-2}$ . Zhao et al. [46]. reported a CuWO<sub>4</sub> catalyst with natural bimetallic sites for high urea productivity (98.5 ± 3.2  $\mu\text{g h}^{-1} \text{mg}^{-1} \text{cat}$ ) with high FE (70.1 ± 2.4%). Additionally, it was established that the electrosynthesis of urea is dependent on the C-N coupling of \*NO<sub>2</sub> and \*CO intermediates on the CuWO<sub>4</sub> surface.

### 2.2.3. Single-Atom Catalysts

Due to their maximum surface atom utilization and controllable physicochemical properties, single-atom catalysts have drawn increasing attention in multiphase catalytic conversion reactions, such as electrochemical CO<sub>2</sub> reduction, N<sub>2</sub> reduction, and O<sub>2</sub> reduction [47-49]. For the first time, Leverett et al. [42] reported on the electrochemical synthesis of urea from CO<sub>2</sub>RR and NO<sub>3</sub><sup>-</sup>RR using Cu SACs. The urea was produced at a current density of -27  $\text{mA cm}^{-2}$  at -0.9 V versus the reversible hydrogen electrode, with a FE of 28%, and demonstrated that the critical parameter's catalytic activity is dependent on \*COOH, which determines the importance of urea. Wei et al.'s work [40] also affirmed the superior performance of Cu single atoms for the electrocatalytic reduction

of  $\text{NO}_3^-$  and  $\text{CO}_2$  for urea synthesis. Cu SACs modified on a  $\text{CeO}_2$  carrier were used to catalyze the synthesis of urea. The average urea yield was  $52.84 \text{ mmol h}^{-1} \text{ gcat}^{-1}$  ( $-1.6 \text{ V}$  vs RHE).

A diatomic catalyst with Fe-Ni bonds has been shown by Zhang et al. [41] to greatly increase the electrochemical urea synthesis's efficiency. Compared to isolated diatomic and monatomic catalysts, the bound Fe-Ni pair served as an efficient site for coordinated adsorption and activation of various reactants, improving the critical C-N coupling both thermodynamically and kinetically. An order of magnitude better results was obtained in urea synthesis than in the previous process, with a high yield of  $20.2 \text{ mmol h}^{-1} \text{ g}^{-1}$  and a corresponding FE of 17.8% [41]. Despite the excellent performance of atomically fractionated catalysts, there are still limitations such as complex preparation procedures, the multiple demands for instruments, and the tendency to aggregate leading to a decrease in catalytic activity. Therefore, the design of single-atom catalysts should focus on utilizing simpler preparation methods and improving the stability of single-atom catalysts.

#### 2.2.4. Carbon-Based Catalysts

The development of carbon-based catalysts has been instrumental in the electroreduction synthesis of urea due to the wide availability and economic feasibility of carbon as compared to metallic elements. Because of their high electrical conductivity and enormous specific surface area, carbon compounds have garnered a lot of interest. Because doping causes a surface charge distribution, doping carbon materials with heteroatoms (such as N, B, and F) is thought to be an effective technique for improving their electrocatalytic characteristics [50,51]. Fluorine-rich surface carbon nanotubes (F-CNTs) with an undamaged inner carbon nanotube wall that facilitates effective charge transfer between the inner and exterior walls were described by Liu et al. [35]. With an efficiency of  $6.36 \text{ mmol h}^{-1} \text{ gcat}^{-1}$  and a FE of 18%, F-CNTs catalyzed the production of urea from  $\text{NO}_3^-$  and  $\text{CO}_2$  under ambient circumstances. In addition to being good electrocatalysts, CNTs are also effective co-catalysts and loading materials for catalytic active sites [52,53]. For instance, a liquid-phase laser irradiation technique was described by Geng's group [33] to create symbiotic graphitic carbon-encapsulated amorphous iron and iron oxide nanoparticles ( $\text{Fe(a)}@\text{C-Fe}_3\text{O}_4/\text{CNTs}$ ) on carbon nanotubes. With a maximal urea production of  $1341.3 \pm 112.6 \mu\text{g h}^{-1} \text{ mgcat}^{-1}$ , a FE of  $16.5 \pm 6.1\%$ , and outstanding stability,  $\text{Fe(a)}@\text{C-Fe}_3\text{O}_4/\text{CNTs}$  demonstrated remarkable electrocatalytic activity for urea synthesis utilizing  $\text{NO}_3^-$  and  $\text{CO}_2$ . It is noteworthy that biomass is renewable and carbon-rich source material, so the conversion of waste biomass into carbon materials during the design of carbon catalysts may be economically feasible and has a broad application prospect. Carbon materials can also be used as co-catalysts to enhance the metal-catalyzed reactivity. Graphene-loaded  $\text{In}_2\text{O}_3$  was created by Mao et al. [54] to demonstrate superior electrocatalytic activity in the production of urea. It was discovered that the dispersion effect of graphene, which completely exposed the active sites of  $\text{In}_2\text{O}_3$ , was primarily responsible for the notable increase in the catalytic activity of  $\text{In}_2\text{O}_3$ .

#### 2.2.5. Defect Engineering Catalysts

It has been reported in the literature that surface defects lead to the generation of off-domains of charge. The ability to change the coordination environment on the surface of metal catalysts facilitates the adsorption and activation of active substances [55–57]. Consequently, several studies have suggested creating oxygen vacancies on the surface of oxides based on metals to aid in the electrocatalytic co-reduction of  $\text{CO}_2$  and  $\text{NO}_3^-$  for the manufacture of urea. For instance, Yu et al. [9] demonstrated effective oxygen vacancy-deficient indium hydroxide electrocatalytic urea synthesis, leading to selective C-N coupling and exceptional electrocatalytic urea synthesis activity. It was discovered that the potential-determining stage of the whole urea production process is  $^*\text{CO}_2\text{NH}_2$  protonation. Consequently, urea synthesis was increased by the application of flawed engineering to lower the energy barrier of  $^*\text{CO}_2\text{NH}_2$  intermediate protonation. Additionally, the poorly designed catalyst yielded  $592.5 \mu\text{g h}^{-1} \text{ mgcat}^{-1}$  of urea and had a high FE of 51.0% [18]. Heteroatom doping can also introduce abundant oxygen vacancies into oxide electrocatalysts. Cao et al. [58] demonstrated that doping low-valent Cu into  $\text{TiO}_2$  nanotubes can produce oxygen vacancy-rich catalysts. The primary cause of the catalyst's high activity is the ability of oxygen vacancies and defects to alter the electronic structure of the active sites on the catalyst surface, which lowers the energy barrier for the conversion of  $^*\text{CO}_2\text{NH}_2$  to  $^*\text{COOHNH}_2$ .

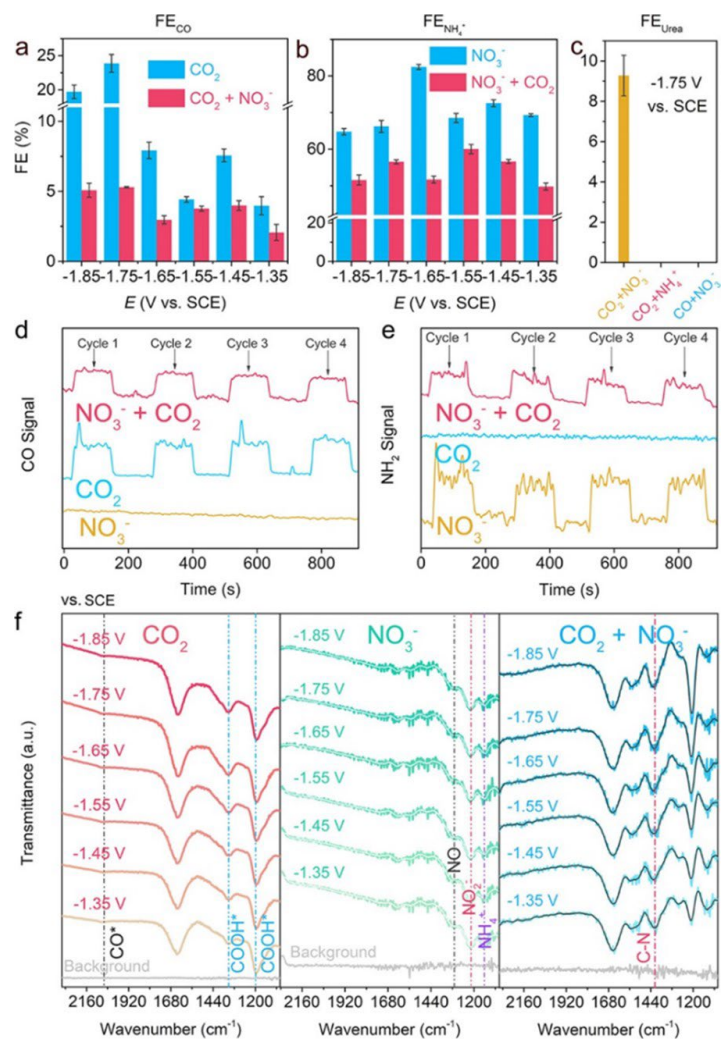
### 2.3. Proposed Reaction Mechanisms

The secret to creating effective electrocatalysts and raising urea yield and selectivity is to examine the C-N coupling reaction mechanism in the electrocatalytic co-reduction of  $\text{CO}_2$  and  $\text{NO}_3^-$  for urea production. These days, density functional theory (DFT) computations and potent in situ characterization techniques are the primary tools used in research on the C-N coupling reaction mechanism. In the  $\text{NO}_3^-$  and  $\text{CO}_2$  co-reduction urea electrosynthesis

reaction system, based on comparative experimental results, most reports indicate that the electrocatalytic CO<sub>2</sub> and NO<sub>3</sub><sup>-</sup> co-reduction synthesis of urea originates from the reaction between \*CO and \*NH<sub>2</sub> intermediate species. The results suggest that the electrocatalyst can facilitate the reaction between CO<sub>2</sub>-to-\*CO and NO<sub>3</sub><sup>-</sup>-to-\*NH<sub>3</sub>, which is effective for urea synthesis [37–39].

Zhang et al. [33] investigated the mechanism of C-N coupling on electrocatalysts Fe(a)@C-Fe<sub>3</sub>O<sub>4</sub>/CNTs by the in-situ Fourier transform infrared (FT-IR) test. Suggesting that certain urea can form Fe<sup>2+</sup>-urea complexes by way of N atoms on the N-H group and oxygen atoms on the C=O group coordinating with Fe<sup>2+</sup>. The in-situ FT-IR measurements showed that the C-N coupling was successfully realized via the coupling process of CO<sub>2</sub> and NO<sub>3</sub><sup>-</sup> catalyzed by Fe(a)@C-Fe<sub>3</sub>O<sub>4</sub>/CNTs. In addition, the authors used DFT calculations to reveal the catalytic reaction mechanism of urea synthesis [45,46,59]. The authors created surface structure models for C+Fe<sub>3</sub>O<sub>4</sub>, carbon-coated crystalline Fe(a)@C, and carbon-coated amorphous Fe (Fe(a)@C) based on the structural properties. Then, it was found that in these three models, \*CO<sub>2</sub> could be reduced to \*CO and \*NO<sub>3</sub> to \*NH<sub>2</sub>. The direct conversion of \*CO<sub>2</sub> to \*CO at the C+Fe<sub>3</sub>O<sub>4</sub> surface is more energetically advantageous than in the other models. As a transition step, \*CO<sub>2</sub> is electrically reduced to \*COOH via a proton-coupled electron transfer (PCET) phase. An important step in the urea-producing process is the production of \*NH<sub>2</sub>, which shows how easy it is to decrease NO<sub>3</sub><sup>-</sup>. As can be seen from the free energy profile for this reaction, the reduction of NO<sub>3</sub><sup>-</sup> to \*NH<sub>2</sub> is a spontaneous process for all three models. The Fe(a)@C site is more likely to produce \*NH<sub>2</sub> since it has the lowest energy. In this case, the coupling of \*NH<sub>2</sub> and \*CO should entail the desorption of the active intermediate and the selection of the coupling site.

The work of Yu et al. [39] also confirms the above idea. The sole carbonaceous product that CO<sub>2</sub> electroreduction produces without nitrate addition is CO. NH<sub>4</sub><sup>+</sup> is the primary nitrogenous product formed by NO<sub>3</sub><sup>-</sup> electroreduction after CO<sub>2</sub> is eliminated. Figure 3a,b demonstrate that FE<sub>CO</sub> and FE<sub>NH<sub>4</sub><sup>+</sup></sub> from the CO<sub>2</sub> + NO<sub>3</sub><sup>-</sup> electroreduction combination are much lower than those from CO<sub>2</sub> and NO<sub>3</sub><sup>-</sup> electroreduction, respectively, pointing to a possible competitive link between the synthesis of CO/NH<sub>4</sub><sup>+</sup> and urea. Notably, substituting CO<sub>2</sub> with CO or NO<sub>3</sub><sup>-</sup> with NH<sub>4</sub><sup>+</sup> did not result in the production of urea (Figure 3c). A series of in situ characterizations were performed in order to reveal the reaction pathway for the electro-synthesis of urea on Cu@Zn. On-line DEMS signal intensity decreased under CO<sub>2</sub> and NO<sub>3</sub><sup>-</sup> conditions (Figure 3d,e), indicating a competitive relationship between CO and NH<sub>2</sub>. Fourier transform infrared spectroscopy, also known as an attenuated complete reflection in situ ATR-FTIR, shows the signals for sole CO<sub>2</sub>, sole NO<sub>3</sub><sup>-</sup>, and mixed electroreduction (CO<sub>2</sub> and NO<sub>3</sub><sup>-</sup>). Typical intermediate peaks were seen under the CO<sub>2</sub> atmosphere (\*CO at 2060 cm<sup>-1</sup> and \*COOH at 1360 and 1210 cm<sup>-1</sup>), as Figure 3f illustrates. Peaks of \*NO (1310 cm<sup>-1</sup>), \*NO<sub>2</sub> (1210 cm<sup>-1</sup>), and NH<sub>4</sub><sup>+</sup> (1140 cm<sup>-1</sup>) are seen during NO<sub>3</sub><sup>-</sup> electroreduction. It is noteworthy that the \*CO peak vanishes under CO<sub>2</sub> and NO<sub>3</sub><sup>-</sup>, whereas the standard C-N bond is seen at 1420 cm<sup>-1</sup>.



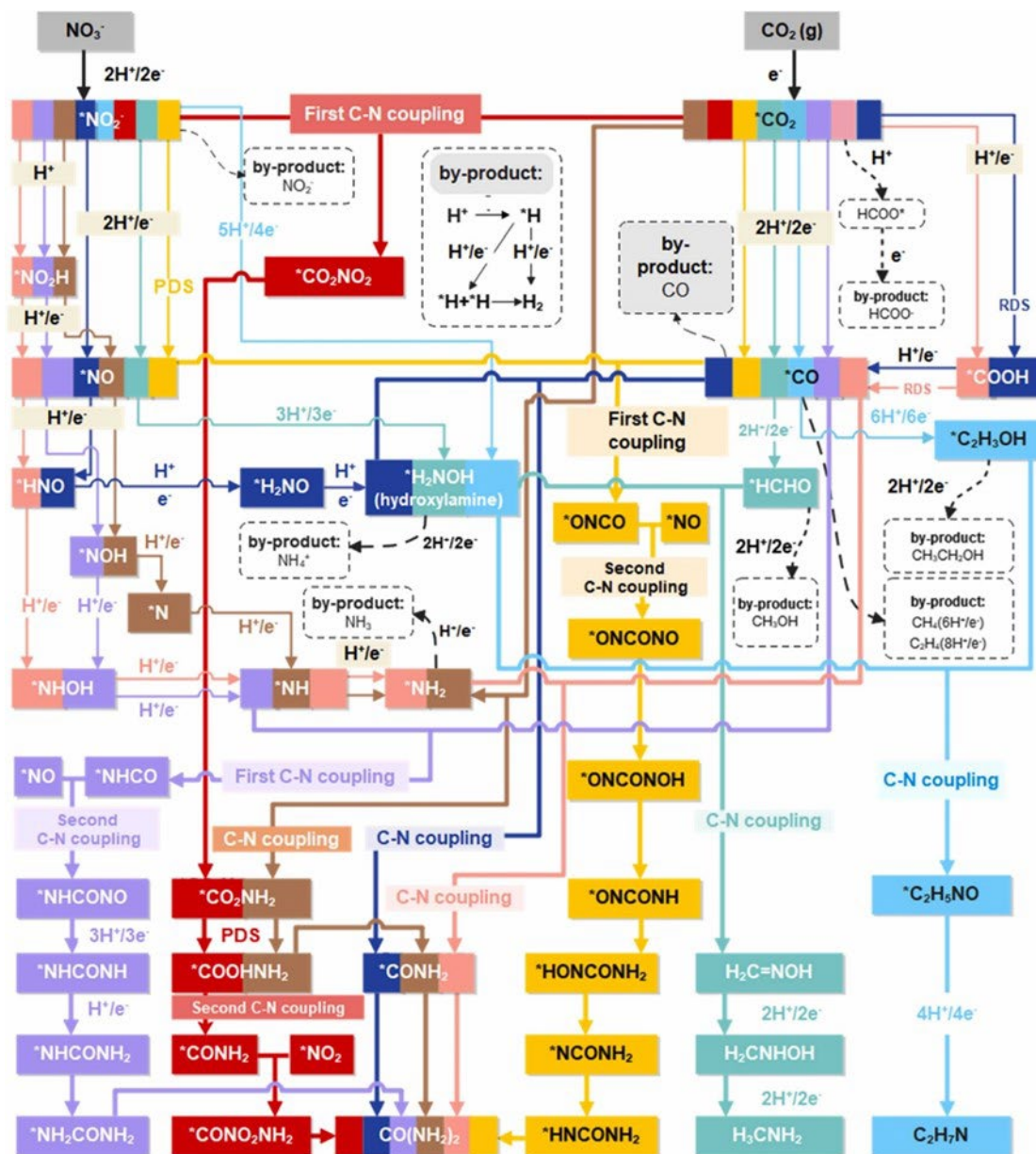
**Figure 3.** (a) FE<sub>CO</sub> for the electrochemical reduction of CO<sub>2</sub> and the mixture. (b) FE<sub>NH<sub>4</sub><sup>+</sup></sub> for the electrochemical reduction of NO<sub>3</sub><sup>-</sup> and the mixture. (c) FE<sub>urea</sub> for the electroreduction of mixtures. DEMS spectra of (d) CO and (e) NH<sub>2</sub> signals. (f) In situ ATR-FTIR spectra [39].

The production of \*CONH<sub>2</sub> as the main intermediate is essential for the synthesis of urea. Qin et al. [37] detected the reaction intermediate by in situ ATR-FTIR to speculate on the reaction pathway of NO<sub>3</sub><sup>-</sup> and CO<sub>2</sub> co-reduction for the synthesis of urea at the MoO<sub>x</sub>/C electrode [37]. At every potential, typical peaks were found at 1420 cm<sup>-1</sup>, indicating the successful production of the C-N bond in the \*CONH<sub>2</sub> intermediate. Subsequently, DFT calculations based on free energy diagrams with the lowest energy routes disclosed the principles of urea generation. More specifically, \*NO<sub>2</sub> intermediates with an adsorption free energy of -2.04 eV are produced when NO<sub>3</sub><sup>-</sup> reduction initiates the urea production process. Interestingly, the \*CO<sub>2</sub>NO<sub>2</sub> intermediate is formed when \*NO<sub>2</sub> and CO<sub>2</sub> are more favorably linked. Then, with a rise in adsorption free energy of 1.38 eV, the hydrogenation of \*CO<sub>2</sub>NO<sub>2</sub> to \*CO<sub>2</sub>NOOH is a potential energy limiting step. This is kinetically more favorable than the potential energy limiting step on MoO<sub>3</sub> (from \*CO<sub>2</sub>NOOH to \*CO<sub>2</sub>NO), with a 1.86 eV rise in free energy. A further reduction route produces a succession of intermediates, \*CO<sub>2</sub>NO, \*CO<sub>2</sub>NHO, \*CO<sub>2</sub>NHOH, \*CO<sub>2</sub>NH, \*CO<sub>2</sub>NH<sub>2</sub> and \*COOHNH<sub>2</sub>, from the CO<sub>2</sub>NOOH intermediate.

Interestingly, the creation of the \*CONH<sub>2</sub> intermediate is thought to be a crucial step in many electrocatalytic systems, even though the protonation of \*COOHNH<sub>2</sub> to \*CONH<sub>2</sub> is an exothermic phase with a free energy loss of -1.77 eV. \*CONO<sub>2</sub>NH<sub>2</sub> is created when \*CONH<sub>2</sub> thermodynamically and spontaneously combines with another \*NO<sub>2</sub> intermediate. The result of this is the creation of \*CO(NH<sub>2</sub>)<sub>2</sub>. As a result, CO(NH<sub>2</sub>)<sub>2</sub> can be produced as a final product with selectivity. Moreover, searching theoretically for effective electrocatalysts to co-reduce CO<sub>2</sub> and NO<sub>3</sub><sup>-</sup> to urea is a plausible strategy. The theoretical study of urea electrosynthesis, which was based on the projector augmented wave approach using the Vienna Ab initio Simulation Package, employed DFT simulations that resembled the urea creation process. The Perdew-Burke-Ernzerh of functional with the generalized gradient approximation and the projector-augmented plane-wave approach was used to model the exchange-correlation potentials and the ion-electron interactions, respectively. In conclusion, there is an ongoing

debate on the specific chemical pathways and crucial intermediates involved in electrocatalytic C-N coupling, and more investigation is required to determine the mechanism behind the production of urea.

As shown in Figure 4, the main mechanism of the electrochemical synthesis of urea is the co-reduction of  $\text{CO}_2$  and  $\text{NO}_3^-$  through a series of PECT and chemical processes (C-N coupling) [60]. The initial conversion of  $\text{CO}_2$  and  $\text{NO}_3^-$  by PECT results in intermediates such as  $^*\text{CO}_2$ ,  $^*\text{CO}$ ,  $^*\text{COOH}$ ,  $^*\text{NO}_2$ ,  $^*\text{NO}$ ,  $^*\text{H}_2\text{NOH}$ ,  $^*\text{NH}$  and  $^*\text{NH}_2$ , which are further transformed to C-N intermediates by C-N coupling. Different intermediates to begin the coupling are a crucial step in the synthesis of urea. C-N coupling may be classified into one-step and two-step methods [18].



**Figure 4.** The general mechanisms in formation of organonitrogen compounds by electrochemical C-N coupling [61].

### 3. Conclusions and Outlook

The production of urea by the electrocatalytic C-N coupling of  $\text{NO}_3^-$  and  $\text{CO}_2$  is an environmentally friendly and sustainable technology that is powered by clean, renewable energy sources and can support the global N and C balance. This study included a summary and presentation of the product testing and evaluation criteria, research progress, design of the electrocatalyst, and reaction mechanism for the electrocatalytic co-reduction of  $\text{NO}_3^-$  and  $\text{CO}_2$  to urea. In most current circumstances, the side reaction still performs better than the C-N coupling. The reaction mechanism of electrocatalytic urea synthesis is still controversial and it is difficult to theoretically guide the design of efficient catalysts. Besides, the active sites of urea formation and the proposed intermediates are still



uncertain. Therefore, an outlook on the existing problems and efforts in the electrocoupling synthesis of urea is summarized.

The practical implementation of urea electrosynthesis still faces several obstacles. For instance, the existence of extremely competitive side reactions such as CO, H<sub>2</sub>, and ammonia results in an unsatisfactory C-N coupling efficiency. The electrochemical synthesis of urea is an integrated multistep process involving proton-coupled electron transfer and C-N coupling steps. Designing catalysts with dual metal sites may be a promising approach as the optimal efficiency for the reduction of CO<sub>2</sub> and NO<sub>3</sub><sup>-</sup> cannot be simultaneously achieved with a single metal active site. Therefore, methods such as surface defect engineering, construction of transition metal alloys or heterojunctions, heteroatom doping, and the use of bimetallic or multimetal catalysts are hopeful avenues for optimizing the electrochemical synthesis of urea. The selectivity and activity of electrocatalytic urea synthesis are significantly restricted by intense competition with the hydrogen evolution reaction (HER) in aqueous solutions. Selecting a suitable electrolyte for efficient electrochemical urea synthesis could significantly improve urea yield and FE<sub>Urea</sub>. Using a high-concentration LiCl solution as the electrolyte, the salt precipitation effect can simultaneously inhibit HER and provide sufficient active hydrogen for the co-reduction of CO<sub>2</sub> and NO<sub>3</sub><sup>-</sup> in urea synthesis. Additionally, ionic liquids with high solubility and affinity for gaseous reaction molecules could be promising electrolyte candidates for electrochemical urea synthesis. Apart from advancing strategies for the rational design of electrocatalysts and electrolyte optimization, reactor configuration remains a bottleneck that needs to be addressed. Liquid flow cells equipped with gas diffusion electrodes are considered effective reactors for gas-solid interface catalytic reactions, providing sufficient contact between gaseous reactants and catalyst surfaces, effectively enhancing the solubility and diffusion rate of gas reaction molecules, thereby improving the electrochemical urea synthesis process.

Further research into the mechanism is necessary for the design of electrocatalysts in the future and for increasing the yield of urea synthesis, particularly in the areas of C-N coupling and by-product generation. In situ characterization techniques play a crucial role in probing the reaction mechanism. Different characterization techniques have different functions, and combining different in situ characterization techniques can make up for the deficiencies existing in a single characterization technique. Consequently, it is anticipated that the development of a network of complimentary in situ characterization methods will offer a more thorough understanding of the C-N coupling reaction mechanism. In order to monitor important intermediates throughout the C-N coupling reaction and identify reactive active sites at the atomic level, more sophisticated in-situ testing methods have been developed. These methods include in-situ Raman spectroscopy, in-situ mass spectrometry, and in-situ Fourier transform infrared spectroscopy. The electrochemical reduction reaction process and the reaction intermediates' transformation mechanism may be thoroughly studied with the aid of these in situ characterization approaches, which can also offer a solid scientific foundation for enhancing the catalysts' catalytic efficacy and product selectivity.

Furthermore, theoretical computations' capacity to investigate the reaction system's atomic-level specifics holds enormous promise for improving our comprehension of how C-N bonds are formed. DFT calculations are widely utilized in the study of multielectron systems. With the advancement of DFT calculations, combining DFT with experimental characterization can be a more effective approach to investigate the thermodynamic properties, active sites, and reaction mechanisms of catalysts for a range of electrocatalytic reactions. Several investigations have demonstrated the critical significance DFT plays in researching reaction processes and forecasting sophisticated catalysts. Convincingly, DFT combined with experiment can eliminate trial and error during catalyst exploration and pave the way for the design of novel advanced electrocatalysts.

**Author Contributions:** L.J.: Methodology, Data curation, Formal analysis, Investigation and Writing—original draft. F.L.: Conceptualization, Formal analysis, Funding acquisition, Methodology, Supervision, Writing-review & editing.

**Funding:** This research was funded by Harbin Institute of Technology, China, grant Number [FRFCU5710053121].

**Acknowledgments:** The authors acknowledge the support from the School of Environment, Harbin Institute of Technology.

**Conflicts of Interests:** The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## References

1. Kawai, E.; Ozawa, A.; Leibowicz, B.D. Role of carbon capture and utilization (CCU) for decarbonization of industrial sector: A case study of Japan. *Appl. Energy* **2022**, *328*, 120183.
2. Ravikumar, D.; Zhang, D.; Keoleian, G.; Miller, S.; Sick, V.; Li, V. Carbon dioxide utilization in concrete curing or mixing might not produce a net climate benefit. *Nat. Commun.* **2021**, *12*, 855.
3. Gao, W.; Liang, S.; Wang, R.; Jiang, Q.; Zhang, Y.; Zheng, Q.; Xie, B.; Toe, C.Y.; Zhu, X.; Wang, J.; et al. Industrial carbon dioxide capture and utilization: State of the art and future challenges. *Chem. Soc. Rev.* **2020**, *49*, 8584–8686.

4. Mac Dowell, N.; Fennell, P.S.; Shah, N.; Maitland, G.C. The role of CO<sub>2</sub> capture and utilization in mitigating climate change. *Nat. Clim. Chang.* **2017**, *7*, 243–249.
5. Chen, C.; Li, S.; Zhu, X.; Bo, S.; Cheng, K.; He, N.; Qiu, M.; Xie, X.; Song, D.; Liu, Y.; et al. Balancing sub-reaction activity to boost electrocatalytic urea synthesis using a metal-free electrocatalyst. *Carbon Energy* **2023**, e345.
6. Wu, Y.; Jiang, Z.; Lin, Z.; Liang, Y.; Wang, H. Direct electrosynthesis of methylamine from carbon dioxide and nitrate. *Nat. Sustain.* **2021**, *4*, 725–730.
7. Li, J.; Zhang, Y.; Kuruvinashetti, K.; Kornienko, N. Construction of C-N bonds from small-molecule precursors through heterogeneous electrocatalysis. *Nat. Rev. Chem.* **2022**, *6*, 303–319.
8. Liu, X.; Jiao, Y.; Zheng, Y.; Jaroniec, M.; Qiao, S.-Z. Mechanism of C-N bonds formation in electrocatalytic urea production revealed by ab initio molecular dynamics simulation. *Nat. Commun.* **2022**, *13*, 5471.
9. Lv, C.; Zhong, L.; Liu, H.; Fang, Z.; Yan, C.; Chen, M.; Kong, Y.; Lee, C.; Liu, D.; Li, S.; et al. Selective electrocatalytic synthesis of urea with nitrate and carbon dioxide. *Nat. Sustain.* **2021**, *4*, 868–876.
10. Yuan, M.; Chen, J.; Bai, Y.; Liu, Z.; Zhang, J.; Zhao, T.; Wang, Q.; Li, S.; He, H.; Zhang, G. Unveiling electrochemical urea synthesis by co-activation of CO<sub>2</sub> and N<sub>2</sub> with Mott-Schottky heterostructure catalysts. *Angew. Chem. Int. Ed.* **2021**, *60*, 10910–10918.
11. Wei, X.; Liu, Y.; Zhu, X.; Bo, S.; Xiao, L.; Chen, C.; Nga, T.T.T.; He, Y.; Qiu, M.; Xie, C.; et al. Dynamic reconstitution between copper single atoms and clusters for electrocatalytic urea synthesis. *Adv. Mater.* **2023**, *35*, 2300020.
12. Wang, H.; Jiang, Y.; Li, S.; Gou, F.; Liu, X.; Jiang, Y.; Luo, W.; Shen, W.; He, R.; Li, M. Realizing efficient C-N coupling via electrochemical co-reduction of CO<sub>2</sub> and NO<sub>3</sub><sup>-</sup> on AuPd nanoalloy to form urea: Key C-N coupling intermediates. *Appl. Catal. B* **2022**, *318*, 121819.
13. Huang, Y.; Wang, Y.; Liu, Y.; Ma, A.; Gui, J.; Zhang, C.; Yu, Y.; Zhang, B. Unveiling the quantification minefield in electrocatalytic urea synthesis. *Chem. Eng. J.* **2023**, *453*, 139836.
14. Li, N.; Gao, H.; Liu, Z.; Zhi, Q.; Li, B.; Gong, L.; Chen, B.; Yang, T.; Wang, K.; Jin, P.; Jiang, J. Metalphthalocyanine frameworks grown on TiO<sub>2</sub> nanotubes for synergistically and efficiently electrocatalyzing urea production from CO<sub>2</sub> and nitrate. *Sci. China Chem.* **2023**, *66*, 1417–1424.
15. Mei, Z.; Zhou, Y.; Lv, W.; Tong, S.; Yang, X.; Chen, L.; Zhang, N. Recent progress in electrocatalytic urea synthesis under ambient conditions. *ACS Sustain. Chem. Eng.* **2022**, *10*, 12477–12496.
16. Martín, A.J.; Veenstra, F.L.P.; Lüthi, J.; Verel, R.; Pérez-Ramírez, J. Toward reliable and accessible ammonia quantification in the electrocatalytic reduction of nitrogen. *Chem Catalysis* **2021**, *1*, 1505–1518.
17. Francis, P.S.; Lewis, S.W.; Lim, K.F. Analytical methodology for the determination of urea: Current practice and future trends. *Trends Anal. Chem.* **2002**, *21*, 389–400.
18. Lv, C.; Lee, C.; Zhong, L.; Liu, H.; Liu, J.; Yang, L.; Yan, C.; Yu, W.; Hng, H.H.; Qi, Z.; et al. A defect engineered electrocatalyst that promotes high-efficiency urea synthesis under ambient conditions. *ACS Nano* **2022**, *16*, 8213–8222.
19. Huang, Y.; Yang, R.; Wang, C.; Meng, N.; Shi, Y.; Yu, Y.; Zhang, B. Direct electrosynthesis of urea from carbon dioxide and nitric oxide. *ACS Energy Lett.* **2022**, *7*, 284–291.
20. Wei, X.; Wen, X.; Liu, Y.; Chen, C.; Xie, C.; Wang, D.; Qiu, M.; He, N.; Zhou, P.; Chen, W.; et al. Oxygen vacancy-mediated selective C-N coupling toward electrocatalytic urea synthesis. *J. Am. Chem. Soc.* **2022**, *144*, 11530–11535.
21. Wang, H.; Jiang, Y.; Li, S.; Gou, F.; Liu, X.; Jiang, Y.; Luo, W.; Shen, W.; He, R.; Li, M. Realizing efficient C-N coupling via electrochemical co-reduction of CO<sub>2</sub> and NO<sub>3</sub><sup>-</sup> on AuPd nanoalloy to form urea: Key C-N coupling intermediates. *Appl. Catal. B* **2022**, *318*, 121819.
22. Huang, Y.; Wang, Y.; Liu, Y.; Ma, A.; Gui, J.; Zhang, C.; Yu, Y.; Zhang, B. Unveiling the quantification minefield in electrocatalytic urea synthesis. *Chemical Engineering Journal* **2023**, *453*, 139836.
23. Chen, G.-F.; Yuan, Y.; Jiang, H.; Ren, S.-Y.; Ding, L.-X.; Ma, L.; Wu, T.; Lu, J.; Wang, H. Electrochemical reduction of nitrate to ammonia via direct eight-electron transfer using a copper-molecular solid catalyst. *Nature Energy* **2020**, *5*, 605–613.
24. Chen, C.; Zhu, X.; Wen, X.; Zhou, Y.; Zhou, L.; Li, H.; Tao, L.; Li, Q.; Du, S.; Liu, T.; et al. Coupling N<sub>2</sub> and CO<sub>2</sub> in H<sub>2</sub>O to synthesize urea under ambient conditions. *Nat. Chem.* **2020**, *12*, 717–724.
25. Kraft, B.; Tegetmeyer, H.E.; Sharma, R.; Klotz, M.G.; Ferdelman, T.G.; Hettich, R.L.; Geelhoed, J.S.; Strous, M. The environmental controls that govern the end product of bacterial nitrate respiration. *Science* **2014**, *345*, 676–679.
26. Chen, F.-Y.; Wu, Z.-Y.; Gupta, S.; Rivera, D.J.; Lambeets, S.V.; Pecaut, S.; Kim, J.Y.T.; Zhu, P.; Finrock, Y.Z.; Meira, D.M.; et al. Efficient conversion of low-concentration nitrate sources into ammonia on a Ru-dispersed Cu nanowire electrocatalyst. *Nat. Nanotechnol.* **2022**, *17*, 759–767.
27. Wang, J.; Chu, L. Biological nitrate removal from water and wastewater by solid-phase denitrification process. *Biotechnol. Adv.* **2016**, *34*, 1103–1112.
28. Wang, Y.; Li, H.; Zhou, W.; Zhang, X.; Zhang, B.; Yu, Y. Structurally disordered RuO<sub>2</sub> nanosheets with rich oxygen vacancies for enhanced nitrate electroreduction to ammonia. *Angew. Chem. Int. Ed.* **2022**, *61*, e202202604.
29. Garcia-Segura, S.; Lanzarini-Lopes, M.; Hristovski, K.; Westerhoff, P. Electrocatalytic reduction of nitrate: Fundamentals to full-scale water treatment applications. *Appl. Catal. B* **2018**, *236*, 546–568.
30. Zhang, X.; Wang, Y.; Liu, C.; Yu, Y.; Lu, S.; Zhang, B. Recent advances in non-noble metal electrocatalysts for nitrate reduction. *Chem. Eng. J.* **2021**, *403*, 126269.
31. De Luna, P.; Hahn, C.; Higgins, D.; Jaffer, S.A.; Jaramillo, T.F.; Sargent, E.H. What would it take for renewably powered electrosynthesis to displace petrochemical processes? *Science* **2019**, *364*, 6438.
32. Shin, H.; Hansen, K.U.; Jiao, F. Techno-economic assessment of low-temperature carbon dioxide electrolysis. *Nat. Sustain.* **2021**, *4*, 911–919.
33. Geng, J.; Ji, S.; Jin, M.; Zhang, C.; Xu, M.; Wang, G.; Liang, C.; Zhang, H. Ambient electrosynthesis of urea with nitrate and carbon dioxide over Iron-based dual-sites. *Angew. Chem. Int. Ed.* **2023**, *62*, e2022109.
34. Li, N.; Gao, H.; Liu, Z.; Zhi, Q.; Li, B.; Gong, L.; Chen, B.; Yang, T.; Wang, K.; Jin, P.; et al. Metalphthalocyanine frameworks grown on TiO<sub>2</sub> nanotubes for synergistically and efficiently electrocatalyzing urea production from CO<sub>2</sub> and nitrate. *Sci. China Chem.* **2023**, *66*, 1417–1424.
35. Liu, X.; Kumar, P.V.; Chen, Q.; Zhao, L.; Ye, F.; Ma, X.; Liu, D.; Chen, X.; Dai, L.; Hu, C. Carbon nanotubes with

- fluorine-rich surface as metal-free electrocatalyst for effective synthesis of urea from nitrate and CO<sub>2</sub>. *Appl. Catal. B* **2022**, *316*, 121618.
36. Shin, S.; Sultan, S.; Chen, Z.-X.; Lee, H.; Choi, H.; Wi, T.-U.; Park, C.; Kim, T.; Lee, C.; Jeong, J.; et al. Copper with an atomic-scale spacing for efficient electrocatalytic co-reduction of carbon dioxide and nitrate to urea. *Energy Environ. Sci.* **2023**, *16*, 2003–2013.
  37. Sun, M.; Wu, G.; Jiang, J.; Yang, Y.; Du, A.; Dai, L.; Mao, X.; Qin, Q. Carbon-anchored molybdenum oxide nanoclusters as efficient catalysts for the electrosynthesis of ammonia and urea. *Angew. Chem. Int. Ed.* **2023**, *62*, e2023019.
  38. Qin, J.; Liu, N.; Chen, L.; Wu, K.; Zhao, Q.; Liu, B.; Ye, Z. Selective electrochemical urea synthesis from nitrate and CO<sub>2</sub> using in situ Ru anchoring onto a three-dimensional copper electrode. *ACS Sustain. Chem. Eng.* **2022**, *10*, 15869–15875.
  39. Meng, N.; Ma, X.; Wang, C.; Wang, Y.; Yang, R.; Shao, J.; Huang, Y.; Xu, Y.; Zhang, B.; Yu, Y. Oxide-derived core-shell Cu@Zn nanowires for urea electrosynthesis from carbon dioxide and nitrate in water. *ACS Nano* **2022**, *16*, 9095–9104.
  40. Wei, X.; Liu, Y.; Zhu, X.; Bo, S.; Xiao, L.; Chen, C.; Nga, T.T.T.; He, Y.; Qiu, M.; Xie, C.; et al. Dynamic reconstitution between copper single atoms and clusters for electrocatalytic urea synthesis. *Adv. Mater.* **2023**, *35*, e2300020.
  41. Zhang, X.; Zhu, X.; Bo, S.; Chen, C.; Qiu, M.; Wei, X.; He, N.; Xie, C.; Chen, W.; Zheng, J.; et al. Identifying and tailoring C-N coupling site for efficient urea synthesis over diatomic Fe-Ni catalyst. *Nat. Commun.* **2022**, *13*, 5337.
  42. Leverett, J.; Tran-Phu, T.; Yuwono, J.A.; Kumar, P.; Kim, C.; Zhai, Q.; Han, C.; Qu, J.; Cairney, J.; Simonov, A.N.; et al. R.K. Tuning the coordination structure of Cu-N-C single atom catalysts for simultaneous electrochemical reduction of CO<sub>2</sub> and NO<sub>3</sub><sup>-</sup> to urea. *Adv. Energy Mater.* **2022**, *12*, 2201500.
  43. Malapit, C.A.; Prater, M.B.; Cabrera-Pardo, J.R.; Li, M.; Pham, T.D.; McFadden, T.P.; Blank, S.; Minteer, S.D. Advances on the merger of electrochemistry and transition metal catalysis for organic synthesis. *Chem. Rev.* **2022**, *122*, 3180–3218.
  44. Sun, H.; Yan, Z.; Liu, F.; Xu, W.; Cheng, F.; Chen, J. Self-supported transition-metal-based electrocatalysts for hydrogen and oxygen evolution. *Adv. Mater.* **2020**, *32*, 1806326.
  45. Luo, Y.; Xie, K.; Ou, P.; Lavallais, C.; Peng, T.; Chen, Z.; Zhang, Z.; Wang, N.; Li, X.-Y.; Grigioni, I.; et al. Selective electrochemical synthesis of urea from nitrate and CO<sub>2</sub> via relay catalysis on hybrid catalysts. *Nature Catalysis* **2023**, *6*, 939–948.
  46. Zhao, Y.; Ding, Y.; Li, W.; Liu, C.; Li, Y.; Zhao, Z.; Shan, Y.; Li, F.; Sun, L.; Li, F. Efficient urea electrosynthesis from carbon dioxide and nitrate via alternating Cu–W bimetallic C–N coupling sites. *Nat. Commun.* **2023**, *14*, 4491.
  47. Hou, C.-C.; Zou, L.; Sun, L.; Zhang, K.; Liu, Z.; Li, Y.; Li, C.; Zou, R.; Yu, J.; Xu, Q. Single-atom Iron catalysts on overhang-eave carbon cages for high-performance oxygen reduction reaction. *Angew. Chem. Int. Ed.* **2020**, *59*, 7384–7389.
  48. Hung, S.-F.; Xu, A.; Wang, X.; Li, F.; Hsu, S.-H.; Li, Y.; Wicks, J.; Cervantes, E.G.; Rasouli, A.S.; Li, Y.C.; et al. A metal-supported single-atom catalytic site enables carbon dioxide hydrogenation. *Nat. Commun.* **2022**, *13*, 819.
  49. Zhu, C.; Fu, S.; Shi, Q.; Du, D.; Lin, Y. Single-atom electrocatalysts. *Angew. Chem. Int. Ed.* **2017**, *56*, 13944–13960.
  50. Kessler, F.K.; Zheng, Y.; Schwarz, D.; Merschjann, C.; Schnick, W.; Wang, X.; Bojdys, M.J. Functional carbon nitride materials design strategies for electrochemical devices. *Nat. Rev. Mater.* **2017**, *2*, 1–17.
  51. Sun, L.; Gong, Y.; Li, D.; Pan, C. Biomass-derived porous carbon materials: Synthesis, designing, and applications for supercapacitors. *Green Chem.* **2022**, *24*, 3864–3894.
  52. Musa, A.B.; Tabish, M.; Kumar, A.; Selvaraj, M.; Khan, M.A.; Al-Shehri, B.M.; Arif, M.; Mushtaq, M.A.; Ibraheem, S.; Slimani, Y.; et al. Microenvironment engineering of Fe-single-atomic-site with nitrogen coordination anchored on carbon nanotubes for boosting oxygen electrocatalysis in alkaline and acidic media. *Chem. Eng. J.* **2023**, *451*, 138684.
  53. Yan, Y.; Miao, J.; Yang, Z.; Xiao, F.-X.; Yang, H.B.; Liu, B.; Yang, Y. Carbon nanotube catalysts: Recent advances in synthesis, characterization and applications. *Chem. Soc. Rev.* **2015**, *44*, 3295–3346.
  54. Mao, Y.; Jiang, Y.; Liu, H.; Jiang, Y.; Li, M.; Su, W.; He, R. Ambient electrocatalytic synthesis of urea by co-reduction of NO<sub>3</sub><sup>-</sup> and CO<sub>2</sub> over graphene-supported In<sub>2</sub>O<sub>3</sub>. *Chinese Chemical Letters* **2023**, *35*, 108540.
  55. Deng, K.; Zhou, T.; Mao, Q.; Wang, S.; Wang, Z.; Xu, Y.; Li, X.; Wang, H.; Wang, L. Surface engineering of defective and porous Ir metallene with polyallylamine for hydrogen evolution electrocatalysis. *Adv. Mater.* **2022**, *34*, 2110680.
  56. Li, W.; Wang, D.; Zhang, Y.; Tao, L.; Wang, T.; Zou, Y.; Wang, Y.; Chen, R.; Wang, S. Defect engineering for fuel-cell electrocatalysts. *Adv. Mater.* **2020**, *32*, 1907879.
  57. Zhu, Y.; Liu, X.; Jin, S.; Chen, H.; Lee, W.; Liu, M.; Chen, Y. Anionic defect engineering of transition metal oxides for oxygen reduction and evolution reactions. *J. Mater. Chem. A* **2019**, *7*, 5875–5897.
  58. Cao, N.; Quan, Y.; Guan, A.; Yang, C.; Ji, Y.; Zhang, L.; Zheng, G. Oxygen vacancies enhanced cooperative electrocatalytic reduction of carbon dioxide and nitrite ions to urea. *J. Colloid Interface Sci.* **2020**, *577*, 109–114.
  59. Gao, X.; Bai, X.; Wang, P.; Jiao, Y.; Davey, K.; Zheng, Y.; Qiao, S.-Z. Boosting urea electrooxidation on oxyanion-engineered nickel sites via inhibited water oxidation. *Nat. Commun.* **2023**, *14*, 5842.
  60. Wei, X.; Wen, X.; Liu, Y.; Chen, C.; Xie, C.; Wang, D.; Qiu, M.; He, N.; Zhou, P.; Chen, W.; et al. Oxygen vacancy-mediated selective C-N coupling toward electrocatalytic urea synthesis. *J. Am. Chem. Soc.* **2022**, *144*, 11530–11535.
  61. Yu, K.; Wang, H.; Yu, W.; Li, S.; Zhang, X.; Bian, Z. Resource utilization of carbon dioxide and nitrate to produce value-added organonitrogen compounds through an electrochemical approach. *Applied Catalysis B: Environmental* **2024**, *341*, 123292.