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### Authors

Ye, Ye

Li, Zhe

Ding, Shichao

et al.

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## Perspective

## Synergistic treatment of carbon dioxide and nitrogen-containing wastewater by electrochemical C-N coupling

Ye Ye,<sup>2,5</sup> Zhe Li,<sup>1,5</sup> Shichao Ding,<sup>3</sup> Jiaju Fu,<sup>1,\*</sup> Hongzhi Liu,<sup>4,\*</sup> and Wenlei Zhu<sup>1,\*</sup>

## SUMMARY

Electrocatalytic CO<sub>2</sub> reduction technology has been considered a promising approach to alleviate the severe environmental and energy issues caused by the anthropogenic over-emission of CO<sub>2</sub>. Coupling CO<sub>2</sub> reduction with nitrogen (N)-pollutants reduction from wastewater to produce higher valued products (e.g., urea, amide, amine, etc.) could significantly extend the application scenarios and product categories of CO<sub>2</sub> reduction technologies. This paper investigates the available CO<sub>2</sub> and N-pollutants sources and summarizes the recent progress of electrocatalytic C-N coupling reactions. Based on the fundamental research, technical concerns for scale-up applications of C-N coupling electrocatalysis are thoroughly discussed. Finally, we prospect the opportunities and challenges with an in-depth understanding of the underlying dominant factors in applying C-N coupling electrocatalysis. Further development in recycling CO<sub>2</sub> and N pollutants via the electrocatalytic C-N coupling process is also discussed.

## INTRODUCTION

With the rapid development of human society, the over-emitted CO<sub>2</sub> from fossil fuel consumption and industrial activity has caused severe environmental issues, e.g., global warming, extreme weather, and sea level rise.<sup>1</sup> At the same time, the accumulation of nitrogen (N) pollutants discharged by fossil fuel combustion and agricultural or industrial activities in water resources also breached the nitrogen cycle balance. Various policies and approaches have been proposed to mitigate these environmental crises by controlling and governing carbon and nitrogen emissions and made great efforts worldwide.<sup>2</sup> However, some carbon and N emissions from human production activities are unavoidable. Hence, converting pollutants to high-value-added chemicals is a promising approach to deal with the conceivable threats in recent years.

The electrochemically converting methods attract significant attention and show tremendous commercial value by taking advantage of mild conditions, being cost-effective, and having the possibility for clean energy storage. Additionally, the electrochemically converting methods could realize the rapid synthesis of products and circumvent the energy-intensive process of conventional industrial reactions.<sup>3</sup> Compared with the sole CO<sub>2</sub>R or N-recycling method, coupling the CO<sub>2</sub>R process with reducing small nitrogenous molecules or ions (e.g., N<sub>2</sub>, NO<sub>2</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>, etc.) could introduce heteroatoms into carbon frameworks. Furthermore, the C-N coupling reaction significantly extends the product diversity and increases the product value of the electrocatalytic process. As listed in Table 1, similar to those of CO<sub>2</sub> reduction and N reduction products, the C-N coupling products showed great market potential with high-valued products like urea, in particular, which can achieve a market value of USD 75.0 Billion.<sup>4</sup>

Briefly, in the C-N coupling reaction, the added N species are firstly converted into N-nucleophilic intermediates (\*NH<sub>3</sub>, \*NH<sub>2</sub>OH, \*N<sub>2</sub>, \*NO<sub>2</sub>, \*NH<sub>2</sub>) and attack the activated C intermediates (\*CO<sub>2</sub>, \*CO, \*COOH, \*CH<sub>2</sub>O) to form C-N bonds<sup>4</sup> (Figure 1). After that, high-value products with heteroatoms would be generated with further reduction, which makes it an alternative way to the energy-intensive technology for producing organonitrogens. More importantly, the nitrogenous substrates can be obtained from N-polluted wastewater. The co-reduction of CO<sub>2</sub> and N species exhibits great potential to optimize the treatment process of N-polluted wastewater and minimize the impacts of N-containing wastewater on the ecological environment and human health.<sup>5</sup>

<sup>1</sup>State Key Laboratory of Pollution Control and Resource Reuse, State Key Laboratory of Analytical Chemistry for Life Science, the Frontiers Science Center for Critical Earth Material Cycling, School of the Environment, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210023, People's Republic of China

<sup>2</sup>Sino-Japan Friendship Center for Environmental Protection, Beijing 100029, People's Republic of China

<sup>3</sup>School of Mechanical and Materials Engineering, Washington State University, Pullman, WA 99164, USA

<sup>4</sup>International Ecological Economy Promotion Association, Beijing 100005, People's Republic of China

<sup>5</sup>These authors contributed equally

\*Correspondence: fujiaju123-123@163.com (J.F.), hongzhi.liu@ieepa.org.cn (H.L.), wenleizhu@nju.edu.cn (W.Z.)  
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**Table 1. Market value of the products from CO<sub>2</sub> reduction, C-N coupling, and N reduction**

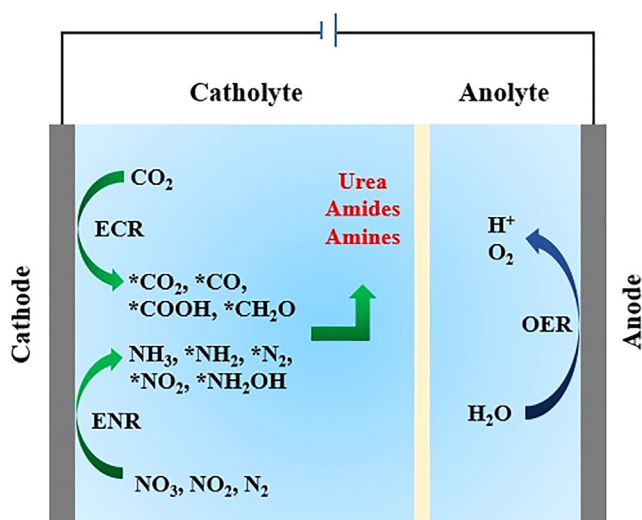
Products	Market value (USD Billion)
Ethylene	162.5
Ethanol	90.3
Urea	75.0
Ammonia	71.98
Methanol	28.74
Acetic Acid	21.39
Methylamine	2.13
Ethylamine	1.26
Acetamide	1.2
n-Propanol	0.299

This paper presents an overview of recent developments in electrochemically C-N coupling approaches and prospects for the synergistic treatment of CO<sub>2</sub> and N-containing wastewater. The electrocatalytic C-N coupling method provides a promising route to create economic values and synergistic treatment of N pollution and carbon emissions.

## CARBON AND N SOURCES FROM POLLUTANTS

### Carbon sources

The statistical investigation of potential carbon and N pollutant sources with a systematic overall plan is essential for the practical applications of electrocatalytic co-reduction of CO<sub>2</sub> and nitrogenous species. According to the reported literature, the excess CO<sub>2</sub> was primarily emitted from industrial activities, power generation, transportation, and agricultural combustions.<sup>6</sup> As exhibited in the carbon emission inventory (Figure 2), the CO<sub>2</sub> emissions of China accounted for a large proportion of the world's total emissions. At the same time, China has made great efforts to control CO<sub>2</sub> emissions.<sup>7-9</sup> During the implementation of the 13<sup>th</sup> Five-Year Plan, China aimed to reduce carbon intensity by 18% compared to 2015 levels and imposed strict standards for all coal-fired power plants. In addition, the 13th Five-Year Plan also set goals to increase forest coverage (23.04%) and forest stock volume (16.5 billion USD) for carbon fixation.<sup>10</sup> In 2020, the carbon intensity was identified to have been reduced by 18.8%, while the forest coverage and forest stock volume also reached the objectives. In the 14<sup>th</sup> Five-Year Plan, the Chinese government updated the related indicators to a higher level, which demonstrates their strong determination to address CO<sub>2</sub> emissions issues.



**Figure 1. The working principle of C-N coupling devices**

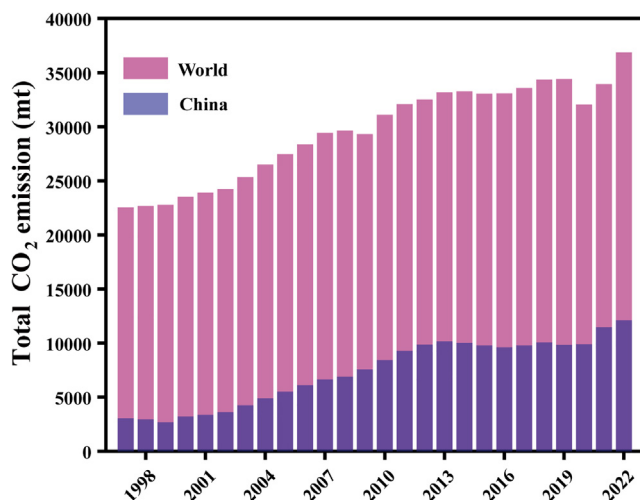


Figure 2. CO<sub>2</sub> emissions from 1997 to 2022, data source from CEAD and World Bank dataset

Behind the issues in governing CO<sub>2</sub> emissions, the massive amount of emitted CO<sub>2</sub> has brought great opportunities in CO<sub>2</sub> recovery and valuable utilization. As a valuable carbon recycling process, anaerobic-generated methane could be recycled in the new-type sewage treatment plant through the combined heat and power (CHP) method accompanied by CO<sub>2</sub> and energy generation. Therefore, the CO<sub>2</sub> emitted from methane combustion could be collected and used as the CO<sub>2</sub> source in CO<sub>2</sub>R or C-N coupling process to realize harmless treatment.

### N sources

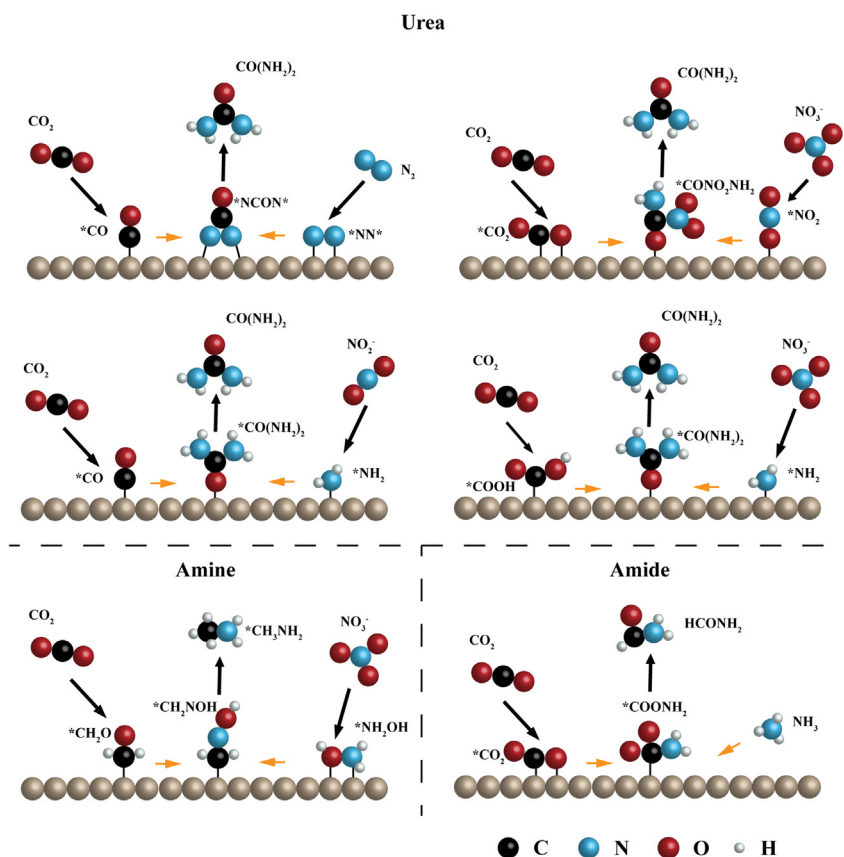
Given the electrochemical C-N coupling process aiming to realize the synergistic treatment of CO<sub>2</sub> and N pollutants, N pollutants' origin is also a critical factor in the system. In recent years, strict regulations have been issued on the maximum concentration of N pollutants (nitrate 50 mg L<sup>-1</sup>, nitrite 0.5 mg L<sup>-1</sup>) in water bodies.<sup>11</sup> As listed in Table 2, the N-containing wastewater was usually generated from industrial activities like fertilizer, stainless steel, or nuclear fuel production, which also emitted large amounts of CO<sub>2</sub> in fumes.<sup>12–16</sup> In addition, during the treatment process of N-containing sewages, N<sub>2</sub> could be simultaneously generated with CO<sub>2</sub> by the denitrifying bacteria, which also could be collected and used as an available N source in the C-N coupling process. Therefore, considering N and CO<sub>2</sub> pollutions are produced simultaneously in many scenarios, setting electrochemical C-N coupling treating plants at the pollution head-stream could be a more efficient approach to achieving emission reductions and avoiding the potential hazards and costs caused by pollutant transportation.

### RECENT FUNDAMENTAL RESEARCH ON ELECTROCHEMICALLY C-N COUPLING

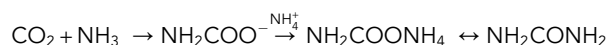
The promising prospect of electrocatalytic C-N coupling in resource recovery and valuable conversions greatly attracted the scientific community. Electrochemically coupling CO<sub>2</sub> and nitrogenous species is a multi-electron transfer process involving various intermediates and multiple reaction pathways, allowing it to produce high-value products. In 2016, a speculative C-N coupling pathway was proposed for urea synthesis<sup>17,18</sup>:

Table 2. N pollutants discharged from the same industrial activities with CO<sub>2</sub>

Industries	N pollutants	NO <sub>3</sub> <sup>-</sup> -N (mg L <sup>-1</sup> )	Reference
Fertilizer	NO <sub>3</sub> <sup>-</sup> , NO <sub>2</sub> <sup>-</sup> , NH <sub>4</sub> <sup>+</sup>	1694–9032	Nair et al., 2007 <sup>12</sup>
Stainless steel	NO <sub>3</sub> <sup>-</sup> , NO <sub>2</sub> <sup>-</sup>	600–1000	Fernández et al., 2008 <sup>13</sup>
Explosive factory	NO <sub>3</sub> <sup>-</sup> , NO <sub>2</sub> <sup>-</sup>	3600	Shen et al., 2009 <sup>14</sup>
Electronic components	NO <sub>3</sub> <sup>-</sup> , NO <sub>2</sub> <sup>-</sup>	200–500	Chang et al., 2019 <sup>15</sup>
Nuclear fuel	NO <sub>3</sub> <sup>-</sup> , NO <sub>2</sub> <sup>-</sup>	10000–40000	Biradar et al., 2008 <sup>16</sup>



**Figure 3. Possible reaction pathways for urea, amine, and amide synthesis by CO<sub>2</sub> and N species in electrocatalytic C-N coupling**



Recent studies demonstrated that the critical step of the co-reduction process should be the nucleophilic attack step: The N-containing nucleophilic intermediates attack the activated carbon center from CO<sub>2</sub>R intermediaries<sup>19–24</sup> (Figure 3). Subsequently, the C-N bond formed and generated heteroatom products like amides, amines, and urea<sup>4</sup> (Table 3).

### Urea synthesis

Frontier research focused on developing high-efficiency electrocatalysts for stabilizing the ketone intermediates during the C-N electro-coupling process. In the 1990s, Furuya proposed forward-looking and inspected the feasibility of electrocatalytic synthesis of urea by using CO<sub>2</sub> and NO<sub>3</sub><sup>−</sup> as reactants, inspiring the following researchers.<sup>36</sup> After that, Wang and his co-worker proposed an attractive approach to produce urea via electrochemical co-reduction of CO<sub>2</sub> and N<sub>2</sub>.<sup>20</sup> This work comprehensively investigates the C-N coupling mechanisms of the electrocatalytic co-reduction of N<sub>2</sub> and CO<sub>2</sub> on CuPd catalysts. Inspired by this work, various electrocatalysts were developed for urea synthesis.<sup>21,25,31,37</sup> The urea synthesis could be realized on various catalysts (Table 3), which induced difficulties in investigating the structure effect on the reaction efficiency. Currently, there is no universal mechanism for electrocatalytic urea synthesis in the C-N coupling system. It can be confirmed that defect engineering shows excellent promise as an approach for achieving efficient urea synthesis in the C-N coupling process. Wang et al. designed an oxygen vacancy-rich CeO<sub>2</sub> electrocatalyst for urea synthesis, which could stabilize intermediate species and realize \*NO coupling with \*CO. Compared to the pristine CeO<sub>2</sub> (~320 mg h<sup>−1</sup> g<sup>−1</sup>), a 3-fold urea yield was reached on the vacancy-rich CeO<sub>2</sub> (943.6 mg h<sup>−1</sup> g<sup>−1</sup>).<sup>32</sup> Although proper defects can improve the urea selectivity of electrocatalysts, the scale-up electrocatalytic urea production on defect-engineered catalysts was rarely reported. The quantity and the location of the vacancies on the catalysts directly impact the

Table 3. Electrocatalytic C-N coupling systems and their reaction parameters

Catalyst	Product	Media	C and N sources	Gas flow rates	Key intermediates	FE %	Operating potential V vs. RHE	Partial current density mA cm <sup>-2</sup>	Total current density mA cm <sup>-2</sup>	Byproducts	Yield rate	Configuration	Reference
Pd1Cu1/TiO <sub>2</sub> -400	Urea	1M KHCO <sub>3</sub>	CO <sub>2</sub> , N <sub>2</sub> (1:1)	30 mL min <sup>-1</sup>	*COOH, *N <sub>2</sub>	8.92	-0.4	3.6	~15	CO, H <sub>2</sub> , NH <sub>3</sub>	3.36 mmol g <sup>-1</sup> h <sup>-1</sup>	GDE	Chen et al., 2020 <sup>20</sup>
Bi-BiVO <sub>4</sub>	Urea	0.1M KHCO <sub>3</sub>	CO <sub>2</sub> , N <sub>2</sub>	N/A	*COOH, *N <sub>2</sub>	12.55	-0.4	0.2	N/A	CO, H <sub>2</sub> , NH <sub>3</sub>	5.91 mmol g <sup>-1</sup> h <sup>-1</sup>	H-CELL	Yuan et al., 2021 <sup>25</sup>
Cu-GS-800	Urea	0.1 M KHCO <sub>3</sub>	CO <sub>2</sub> , NO <sub>3</sub> <sup>-</sup>	N/A	*CO, *NH <sub>2</sub>	28	-0.9	N/A	27	NH <sub>3</sub> , CO, HCOOH	1840 μg h <sup>-1</sup> mg <sup>-1</sup> cat	H-CELL	Leverett et al., 2022 <sup>26</sup>
F-CNT-300	Urea	0.1 M KNO <sub>3</sub>	CO <sub>2</sub> , NO <sub>3</sub> <sup>-</sup>	30 mL min <sup>-1</sup>	*CO, *NH <sub>2</sub>	18	-0.65	0.3	N/A	NH <sub>3</sub>	6.36 mmol h <sup>-1</sup> g <sup>-1</sup> cat.	H-CELL	Liu et al., 2022 <sup>10</sup>
Cu@Zn Nanowires	Urea	0.2 M KHCO <sub>3</sub>	CO <sub>2</sub> , NO <sub>3</sub> <sup>-</sup>	20 mL min <sup>-1</sup>	*CO, *NH <sub>2</sub>	9.28	-1.02	~3	N/A	NH <sub>4</sub> <sup>+</sup> , NO <sub>2</sub> <sup>-</sup> , CO, H <sub>2</sub> , N <sub>2</sub>	7.29 μmol cm <sup>-2</sup> h <sup>-1</sup>	H-CELL	Meng et al., 2022 <sup>27</sup>
V <sub>o</sub> -InOOH	Urea	0.1 M KNO <sub>3</sub>	CO <sub>2</sub> , NO <sub>3</sub> <sup>-</sup>	20 mL min <sup>-1</sup>	*CO <sub>2</sub> , *NO <sub>2</sub>	51	-0.5	N/A	N/A	NH <sub>3</sub> , H <sub>2</sub> , NO <sub>2</sub> , CO	592.5 μg h <sup>-1</sup> mg <sup>-1</sup> cat	H-CELL	Lv et al., 2022 <sup>21</sup>
(Fe(a)@C-Fe <sub>3</sub> O <sub>4</sub> /CNTs	Urea	0.1 M KNO <sub>3</sub>	CO <sub>2</sub> , NO <sub>3</sub> <sup>-</sup>	N/A	*CO, *NH <sub>2</sub>	16.5 ± 6.1	-0.65	N/A	~4	NH <sub>3</sub> , NO <sub>2</sub>	1341.3 ± 112.6 μg h <sup>-1</sup> mg <sup>-1</sup> cat	H-CELL	Geng et al., 2023 <sup>28</sup>
Ru-Cu CF	Urea	0.1 M KNO <sub>3</sub>	CO <sub>2</sub> , NO <sub>3</sub> <sup>-</sup>	20 mL min <sup>-1</sup>	*COOH, *NH <sub>2</sub>	25.4	-0.13	N/A	~10	NH <sub>4</sub> <sup>+</sup> , NO <sub>2</sub> <sup>-</sup> , HCOOH, CO	151.6 μg h <sup>-1</sup> cm <sup>-2</sup>	H-CELL	Qin et al., 2022 <sup>29</sup>
Cu-TiO <sub>2</sub> -Vo	Urea	0.2 M KHCO <sub>3</sub>	CO <sub>2</sub> , NO <sub>2</sub> <sup>-</sup>	N/A	*CO, *NH <sub>2</sub>	43.10	-0.4 V	N/A	~8	NH <sub>3</sub> , N <sub>2</sub> , CH <sub>4</sub> , CO, H <sub>2</sub>	20.8 μmol	H-CELL	Cao et al., 2020 <sup>30</sup>
XC72R-AuPd	Urea	0.075 M KHCO <sub>3</sub>	CO <sub>2</sub> , NO <sub>3</sub> <sup>-</sup>	N/A	*CO, *NO	15.60	-0.4 V	N/A	N/A	NH <sub>3</sub> , CO, H <sub>2</sub> , NO <sub>2</sub> <sup>-</sup> , NH <sub>2</sub> OH	204.2 μg · h <sup>-1</sup> · mg <sup>-1</sup> · h <sup>-1</sup>	H-CELL	Wang et al., 2022 <sup>18</sup>
B-FeNi-DASC	Urea	0.1 M KHCO <sub>3</sub>	CO <sub>2</sub> , NO <sub>3</sub> <sup>-</sup>	30 mL min <sup>-1</sup>	*COOH, *NH	17.80	-1.5 V	N/A	~42	CO, NH <sub>3</sub>	20.2 mmol h <sup>-1</sup> g <sup>-1</sup>	H-CELL	Zhang et al., 2022 <sup>31</sup>
Vo-CeO <sub>2</sub> -750	Urea	0.1 M KHCO <sub>3</sub>	CO <sub>2</sub> , NO <sub>3</sub> <sup>-</sup>	50 mL min <sup>-1</sup>	*CO, *NO	1	-1.6V	N/A	~40	NH <sub>3</sub>	943.6 mg g <sup>-1</sup> · h <sup>-1</sup>	H-CELL	Wei et al., 2022 <sup>32</sup>
In(OH)3-S	Urea	0.1 M KNO <sub>3</sub>	CO <sub>2</sub> , NO <sub>3</sub> <sup>-</sup>	20 mL min <sup>-1</sup>	*CO <sub>2</sub> , *NO <sub>2</sub>	53.40	-0.6 V	0.3	N/A	NH <sub>3</sub> , CO, HCOOH	533.1 μg h <sup>-1</sup> mg <sup>-1</sup> cat	H-CELL	Lv et al., 2021 <sup>21</sup>

(Continued on next page)

Table 3. Continued

Catalyst	Product	Media	C and N sources	Gas flow rates	Key intermediates	FE %	Operating potential V vs. RHE	Partial current density mA cm <sup>-2</sup>	Total current density mA cm <sup>-2</sup>	Byproducts	Yield rate	Configuration	Reference
CoPc-NH <sub>2</sub> /CNT	CH <sub>3</sub> NH <sub>2</sub>	0.1 M KHCO <sub>3</sub>	CO <sub>2</sub> , NO <sub>3</sub> <sup>-</sup>	N/A	*HCHO, *NH <sub>2</sub> OH	13	-0.92 V	3.4	~20	H <sub>2</sub> , CO, CH <sub>3</sub> OH, NO <sub>2</sub> , NH <sub>2</sub> OH, NH <sub>3</sub> , CH <sub>2</sub> =NOH, CH <sub>3</sub> NHOH	N/A	H-CELL	Wu et al., 2021 <sup>23</sup>
OD Cu	CH <sub>3</sub> CH <sub>2</sub> NH <sub>2</sub>	1 M KHCO <sub>3</sub>	CO <sub>2</sub> , NO <sub>3</sub> <sup>-</sup>	N/A	*CH <sub>3</sub> CHO, *NH <sub>2</sub> OH	0.30	-1 V	0.26	70	H <sub>2</sub> , CH <sub>4</sub> , CO, C <sub>2</sub> H <sub>4</sub>	N/A	H-CELL	Tao et al., 2022 <sup>33</sup>
Cu-Hg	Glycine	15 wt % H <sub>2</sub> SO <sub>4</sub>	Oxalic acid NO <sub>3</sub> <sup>-</sup>	N/A	*OHCCOOH, *NH <sub>2</sub> OH	43	-1.2 V	39	90	glycolic acid, glyoxylic acid, H <sub>2</sub>	45.5% oxalic acid transformed to glycine	H-CELL	Kim et al., 2021 <sup>34</sup>
Cu	CH <sub>3</sub> CONH <sub>2</sub>	1 M KOH	CO and NH <sub>3</sub>	5 mL min <sup>-1</sup> 10 mL min <sup>-1</sup>	*C=C=O, NH <sub>3</sub>	38	-0.68 V	114	~300	n-propanol, acetate, ethanol, ethylene, H <sub>2</sub>	N/A	GDE	Jouny et al., 2019 <sup>35</sup>
Pt	CH <sub>3</sub> CONH <sub>2</sub>	0.5M NaHCO <sub>3</sub>	CH <sub>3</sub> OH, NH <sub>3</sub>	N/A	*CH <sub>2</sub> O, NH <sub>3</sub>	40.39	N/A	N/A	100	HCOO <sup>-</sup>	50 μmol cm <sup>-2</sup> h <sup>-1</sup>	Membrane-free cell	Meng et al., 2022 <sup>27</sup>

adsorption behaviors of carbon or N intermediates. Therefore, the structure-activity relationship between defects and active sites could be a key factor for scaled-up urea electrocatalytic synthesis.

### Amine synthesis

Amine products, including methylamine, ethylamine, and aromatic amines, were also successfully synthesized.<sup>23,33,38</sup> These advanced research comprehensively understand the reaction pathways for producing various products between the generated  $\ast\text{NH}_2\text{OH}$  intermediate and  $\ast\text{R-CHO}$  intermediates. Although the amines were successfully synthesized by the electrocatalytic C-N coupling method, the Faradaic efficiency (FE) of target products is still at a lower level (<20%). Since the mechanism of this cascade catalysis has been well understood, feedstock selection is an efficient way to optimize the interactions between intermediates during the C-N process. By utilizing the carbonyl-hydroxylamine coupling mechanism, a highly efficient method was proposed to produce glycine by the co-reduction of 0.25 M oxalic acid and 0.25 M nitrate in a 15 wt %  $\text{H}_2\text{SO}_4$  solution with over 40% FE and a current density of  $90 \text{ mA cm}^{-2}$ .<sup>34</sup> This gives us a new vision of producing more complex organonitrogen compounds by the hydroxylamine-carbonyl reaction. *With further investigation of the electrocatalytic  $\text{CO}_2\text{R}$  technique, more organic compounds containing carbonyl or carboxyl groups will be thermodynamically favorable and mass-produced. Amino acid with specific chiral structures is expected to be synthesized through the C-N coupling electrocatalysis at the appointed time.*

### Amides synthesis

Amide synthesis is meaningful due to its appearance in the medical and pharmaceutical industries. Jiao et al. reported the electrocatalytic C-N bond formation from CO and  $\text{NH}_3$  to produce acetamide.<sup>35</sup> The nearly 40% FE with a partial current density of  $114 \text{ mA cm}^{-2}$  at  $-0.68 \text{ V vs. RHE}$  (reversible hydrogen electrode) in their proposed system indicated that the electrochemical C-N coupling holds enormous promise in the synergistic treatment of carbon gases and N-containing wastes. Further, formamide and acetamide were obtained on Cu-based catalysts using  $\text{CO}_2$  as the carbon source. However, the FE and the partial current density (0.4%,  $0.2 \text{ mA cm}^{-2}$  for formamide and 10%,  $2.2 \text{ mA cm}^{-2}$  for acetamide) were relatively low owing to the weak adsorption of  $\ast\text{COO}$ .<sup>24</sup> Notably, effective electrocatalytic amide synthesis was barely reported using  $\text{CO}_2$  and  $\text{NO}_3^-$  (or  $\text{N}_2$ ) as the feedstocks. Except for the difficulties in the *in situ* generation of suitable carbon intermediates during the electrocatalytic process, nitrogenous species also need to be converted into  $\text{NH}_3$ , whose selectivity and yield of  $\text{NH}_3$  were limited by the complex reactions in the C-N coupling system. Currently, the N source in electrocatalytic amide synthesis mainly relies on amine reagents. Since the nucleophilic reagents in electrocatalytic amide synthesis are in "ready-made" form, optimizing C-intermediate properties (intermediate type, stability, and surface adsorption energy) has played a key role in electrocatalytic amide synthesis.

The method for direct synthesis of amides by  $\text{CO}_2$  and  $\text{NO}_3^-$  is of great significance to give us a deeper understanding of the reaction pathways and C-N coupling mechanism. In our opinion, the key challenge is to improve the stability of amide-oriented carbon intermediates and reduce the competition of N reduction reactions in the reaction system. To enhance the efficiency of amide formation, the reaction system can be improved from two aspects: (1) designing high-efficiency catalysts for stabilizing amide-oriented carbon intermediates from  $\text{CO}_2$  and enriching the local N intermediates could increase the molar ratio of amide-oriented carbon intermediates and (2) designing a membrane-based dual-cathode reactor for optimizing the mass transfer of  $\text{NO}_3^-$  and  $\text{CO}_2$  feedstocks and the N/C intermediates for producing amides and regulating the local microenvironment on the catalytic interfaces could improve the activity for converting  $\text{CO}_2$  to amide-oriented carbon intermediates and nitrate to ammonia with effective ammonia transfer.

The fundamental study for electrocatalytic C-N coupling is still at the primary stage. Thus, the employed  $\text{CO}_2$  and N species are generally used with at least analytical grade purity, while the purity effects of the C or N sources were not investigated. However, the purity of N sources in N-containing wastewater may affect the C-N coupling efficiency due to competitive reactions or catalyst poisoning.<sup>39</sup> Since current works aim to reduce the hazards caused by C or N pollutants and bring valuable organonitrogen products, the reaction performances and selectivity of the catalyst in relatively impure feedstocks should be considered as an evaluation criterion when designing catalysts. The selectivity of organonitrogens could be adjusted by tuning the molar ratio of  $\text{CO}_2$  and N pollutants. It has been reported that the selectivity of organonitrogen should depend on the competition between carbon reduction and N reduction and the kinetics of the C-N bond formation step. The molar ratio of carbon and N feedstocks could affect the local concentration



**Table 4. Detectable intermediates or variations by the *in situ* characterization methods**

Methods	Detectable intermediates or variations	Reference
<i>in situ</i> DEMS	CO, CH <sub>4</sub> , C <sub>2</sub> H <sub>4</sub> , NO <sub>2</sub> , NO, NH <sub>2</sub> OH, NH <sub>3</sub>	Clark and Bell, 2018 <sup>48</sup> ; Wang et al., 2020 <sup>45</sup>
<i>in situ</i> ESR	·H, *C	Li et al. 2020 <sup>42</sup>
<i>in situ</i> FTIR	N-H, H-N-H, OCO, NH <sub>2</sub> , C=O, C-O, C-N,	Lv et al., 2021 <sup>21</sup>
<i>in situ</i> Raman	Adsorbed *CO, C≡O, C-H, the valence of metal catalyst	Dutta et al., 2015 <sup>43</sup> ; Gao et al., 2019 <sup>44</sup>
<i>in situ</i> XAS	Zn-O bond, Cu-N bond, Cu-Cu bond, Pd-H bond	Wang et al., 2020 <sup>45</sup>

of the intermediates, thus influencing product selectivity. For instance, by tuning the molar ratios of CH<sub>3</sub>OH to NH<sub>3</sub> from 1:1 to 5:1, the performance of formamide synthesis showed significant improvement when using boron-doped diamond as the catalyst.<sup>40</sup>

For future applications, developing an industrial chain for the electrocatalytic synthesis of urea, amine, and amide can provide a comprehensive approach to organonitrogen synthesis. The CO and NH<sub>3</sub> byproducts from electrocatalytic urea and amine synthesis can be used as carbon and N feedstocks for amide synthesis. Moreover, the obtained amine from electrocatalytic C-N coupling can be employed as the N source in the synthetic approach of amides to get more complex organonitrogen compounds. With the development of the nitrate reduction (NITR) technique, the recycled NH<sub>3</sub> is also a promising N source for electrocatalytic amide synthesis.

## TECHNOLOGY BASIS FOR REALIZING INDUSTRIAL C-N COUPLING ELECTROCATALYSIS

Although numerous materials have been proposed as effective C-N coupling catalysts to produce organonitrogen on a lab scale, considering technical issues is beneficial to enhance the feasibility of the scale-up applications.

### Operando technologies for intermediates quantification

One of the most significant preconditions to realize industrial-level C-N coupling electrocatalysis is improving the catalyst selectivity. To achieve this goal, the electrochemical pathway of the C-N coupling process needs to be revealed. The regulation mechanisms could be uncovered by monitoring reaction intermediates, radicals, and electronic structure variations of catalytic sites.<sup>41</sup> Given that the intermediates were short lived and highly reactive during the electrochemical process, advanced operando characterization techniques are required to identify the structure of intermediates and observe their catalytic behaviors on the catalytic interfaces. Generally, the analysis was performed by single or combined *in situ* characterization methods depending on the types of intermediates (Table 4). Hydrogen radical (·H) could be trapped by 5,5-dimethyl-1-pyrroline-*n*-oxide (DMPO) and obtained a longer lifetime owing to the formation of DMPO-H, which showed a nine peaks signal with 1:1:2:1:2:1:2:1:1 intensity ratio as the characteristic expression in the electron spin resonance (ESR) spectrum. The *in situ* ESR can assist researchers in verifying the behavior of (·H) in different reaction conditions, allowing for a better understanding of the generation of ·H during the electrochemical reduction process.<sup>42</sup> Except for activated hydrogen, monitoring reactive intermediates and interactions on the surface of catalysts is also an efficient way to investigate the reaction mode of the electrocatalytic process. For example, the *in situ* Fourier transform infrared spectroscopy (FTIR spectroscopy) could sensitively observe the variations of characteristic intermediates, revealing the possible electrocatalytic reaction pathways. By changing reaction time or applied voltage, the vibration and rotation bands of characteristic intermediates will undergo appearance, enhancement, disappearance, or displacement on the spectra, which provide pivotal information to perfect the reaction pathway and kinetics.<sup>21</sup> In addition, the surface property of catalysts, like valence state changes and interactions between intermediates and active sites, could be monitored through the *in situ* Raman spectra.<sup>43,44</sup> To further verify the reaction steps, *in situ* X-ray absorption spectroscopy (XAS) can be used as an effective tool to monitor the electronic structure changes of electrocatalysts during the reaction process, giving insights into the real-time information on the interactions between the intermediates and active sites.<sup>45–47</sup> Except for the above technologies, differential electrochemical mass spectrometry (DEMS) is also an effective tool for identifying the products or intermediates of continuous electrocatalytic reactions by analyzing mass spectra or mass spectrometric voltammograms. Based on the characteristic mass-charge ratio, it can monitor volatile products such as CO, CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, NO<sub>2</sub>, NO, NH<sub>2</sub>OH, and NH<sub>3</sub>.<sup>48,49,50</sup> The intermediates and the reaction pathway can be deduced by combining theoretical calculations. However, individual *in situ* characterization still has some limitations in giving comprehensive information about the electrocatalytic system.

The rational combination of *in situ* and other characterization techniques should be established based on the requirements of mechanistic validation.

### Energy sources from renewable energy

Given the cost reductions, technological breakthroughs, and the proportion increase in the future energy supply chain, renewable energy can be a reliable and cost-effective source for driving large-scale C-N coupling electrocatalysis. Among the available renewable energy sources, photovoltaic power is the safest and most suitable energy source associated with the electrochemical C-N coupling equipment. Compared with other renewable energy devices, photovoltaic power devices are composed of electronic components without complex mechanical parts. Thus, a photovoltaic power device is beneficial for installation and maintenance, which could also provide clean, safe, and renewable energy for C-N coupling treatment plants. With the development of photovoltaic technology, photovoltaic equipment with higher conversion efficiency is expected to be developed further to reduce the floor area of the power supply facilities.

### CO<sub>2</sub> from carbon capture and storage (CCS)

The capture and storage of CO<sub>2</sub> are critical to reducing carbon emissions and providing opportunities for CO<sub>2</sub> utilization.<sup>51</sup> In the C-N electrocatalytic coupling process, the purity of gas-phase feedstocks would significantly affect the productivity of organonitrogens. A complex gas composition could induce side reactions and poison the electrocatalysts.<sup>52</sup> Attributed to developing some of the individual components for CO<sub>2</sub> capture, the purity of CO<sub>2</sub> from the CCS system can be ensured with further investments. For example, direct air capture and storage (DACs) technology is a practical approach to capturing CO<sub>2</sub> from the atmosphere.<sup>53</sup> In a DACs system, air passing through a chemical filter driven by an industrial-scale fan could trap the low-concentration CO<sub>2</sub> and send other air components back into the atmosphere. The captured CO<sub>2</sub> with high purity can then be released by heating and directly used in the C-N coupling system. Apart from DACs technology, post-combustion CO<sub>2</sub> capture technology and pre-combustion CO<sub>2</sub> capture technology can also be conducted to supply constant carbon sources for the scale-up C-N coupling system.

For practical application in C-N coupling electrocatalysis systems, the feasibility of CCS depends on the scale-up operation and the technology costs reduction. Currently, the cost issue is the main factor preventing the popularization of CO<sub>2</sub> collection and storage technology.<sup>54</sup> Although the synergistic treatment of CO<sub>2</sub> and N-containing wastewater from the same industrial activities may solve the storage issues, the innovation of the CCS process plays a crucial role in reducing costs in practical applications.

### Wastewater pretreatment technologies

The coexistence of multiple pollutants in wastewater may cause strong side reactions or catalysts poisoning, demanding appropriate pretreatment technologies. For C-N coupling electrolysis, the pretreatment of N-containing wastewater is beneficial to reduce the interferences of organic and metallic impurities. The established gravity separation, coagulation/flocculation, filtration separation, and adsorption methods provide a technological basis for N-containing wastewater pretreatment.<sup>55,56</sup> Pretreatment could eliminate suspensions, heavy metals, dissolved organic materials, and floating oil. Furthermore, other N-containing wastewater treatment methods can also provide N sources for electrochemical C-N coupling. Generally, the N removal efficiency of A/O or A<sup>2</sup>/O can only reach 70%–80%. According to the technical characteristics of the A/O or A<sup>2</sup>/O process, the nitrification liquid from the oxidation tank is promising to be used as the pretreated nitrate source for electrochemical C-N coupling. With the further elimination of organic pollutants in the aerobic tank and the ammoniacal N transformation through nitrifying bacteria, nitrate concentration and purity in nitrification liquid will gradually increase. The direct use of nitrification liquid from the aerobic tank also provides a new approach to improving N removal efficiency since the activity of anaerobic bacteria in an anoxic tank is restricted in the presence of highly concentrated nitrate. In this case, using A/O or A<sup>2</sup>/O as a pretreatment method for N-containing wastewater solves the relatively low N removal rate of these two methods and provides high-quality N sources for electrochemical C-N coupling.

### Smart design of advanced devices

An advanced device should be able to boost the target reactions and allow for scale-up applications. Shao et al. proposed a solar-driven single-cell electrolysis device equipped with an electrolytic cell chamber, liquid pump, circulating liquid barrel, and electrode.<sup>40</sup> The scale-up device exhibited excellent

performance in synthesizing formamide by using methanol and ammonia as the feedstocks, with the highest FE of 33.5% at  $120 \text{ mA cm}^{-2}$ , providing a compelling experimental validation for the future implementation of electrocatalytic C-N coupling with renewable energy sources. In addition, the mass transfer process is another vital issue for practical applications.<sup>57</sup> The imperceptible mass transfer resistance would become prominent under industrial operating conditions, requiring the design of suitable cell units based on the C-N coupling process. To date, the membrane electrode assemblies (MEAs) technology is considered a promising approach to overcoming the barrier of substrate mass transfer, modulating the local environments of catalytic interfaces, and adapting industrial scenarios for various electrocatalytic reactions.<sup>58</sup> MEA could enable ionic transportation and act as a barrier to prevent the crossover of gas and electron. The gas, ions, and electrons could be gathered at the triple-phase boundary (catalyst surface) to improve the mass transfer efficiency.<sup>59</sup> Moreover, regulating catalyst distribution and flow channel structures on MEAs could further optimize the mass transfer and microenvironment on the catalytic interfaces at higher current densities. Thus, the overall performance of the electrocatalytic system could be promoted. From future perspectives, the MEAs fabricating technologies should be further investigated, focusing on the high catalyst utilization, low cost, and long-life characteristics. Once the technology is matured and conforms to application standards, the reactors with modularized MEA could realize scale-up C-N coupling electrocatalysis.

### Coupling energy-efficiency anode reactions

The rational employment of the anodic oxidation reaction is a promising approach for efficiently utilizing the whole electrolytic cell. In most electrolyzers, oxygen evolution reaction (OER) is the primary anodic reaction and is recognized as another critical factor in the overall performance of electrolysis.<sup>27</sup> Typically, the anodic OER requires a high applied potential and can induce a high bias voltage in the electrocatalytic cell. A suitable OER catalyst could reduce the bias voltage and energy consumption. Currently, the widely recognized effective OER catalysts are iridium and ruthenium oxides. However, the scarcity and high cost severely limit their large-scale application. In this case, numerous non-noble metal OER catalysts were developed and showed significant improvement in the OER efficiency. This allows for a highly efficient and stable anode reaction in the electrolytic cell.<sup>60,61</sup> Furthermore, on the anode side, introducing a suitable anode catalyst could trigger oxidative reactions with specific directions, which is beneficial to reduce the high bias voltage and energy consumption. For instance, Zhang et al. reported the electrocatalytic conversion of methanol and ammonia into high-valued organonitrogen with high selectivity and FE.<sup>27</sup> As for the anode side, the methanol was oxidized to an aldehyde-like intermediate by a Pt-Ti catalyst and coupled with  $\text{NH}_3$  through the nucleophilic attack. By utilizing the oxidative property of the anodic reaction, wastewater with organic pollutants can be effectively treated through the "advanced electrochemical oxidation processes". However, when using multiple organic pollutants containing wastewater as the anode electrolyte, the stability of the electrolytic cell should be a concern. The degradation of different organic pollutants may induce various bias voltages to affect the C-N coupling efficiency on the cathode side, which also requires cathode catalysts to achieve effective catalysis in a wide voltage range. The carbon emissions from anodic reactions could be captured by the CCS system, thus providing another carbon source for the cathodic C-N coupling process.

### OUTLOOKS AND PERSPECTIVES

Considering the lately proposed policy by the Chinese government, the electrocatalytic C-N coupling technology aligns with the goals of balancing the environmental, climate, and economic gains during the treatment process.<sup>62</sup> For environmental and climatic considerations, the  $\text{CO}_2$  and N pollutants from industrial activities could be controlled at the source by the electrocatalytic C-N coupling process. Besides, high-value-added organonitrogen products of the C-N coupling between  $\text{CO}_2$  and N pollutants like urea, amides, and amines could bring tremendous economic benefits. The market size for amines and urea was predicted to reach tens of billions of dollars and has enormous potential and broad market prospects.<sup>63,64</sup> Therefore, recycling  $\text{CO}_2$  and N pollutants by electrocatalytic C-N coupling has a reasonable option in pollution control applications and can be conducive to mitigating climate change and water pollution control.

According to the studies mentioned above, the electrocatalytic C-N coupling process research is still in the early stage. Fundamental aspects, including the reaction mechanisms, structure-activity relationship of catalytic sites, and the microenvironment of the catalytic interfaces, still need systematic investigation to support the practical application. As the achievable target for industrial-level electrolysis, the energy efficiency should reach at least 40% with a current density larger than  $500 \text{ mA cm}^{-2}$ . However, at present, most studies

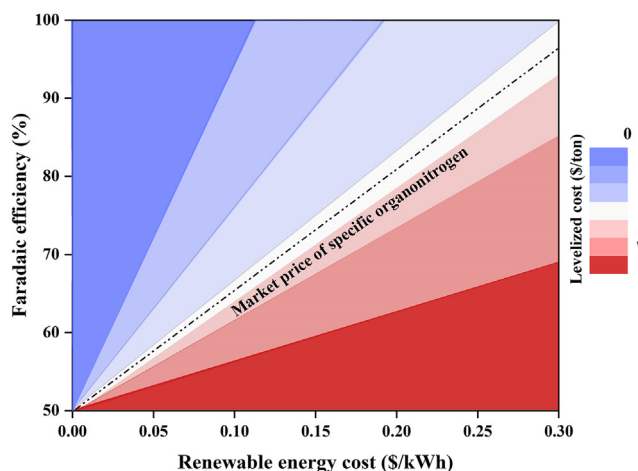
sacrificed their current density to improve the FE (Table 3). Challenge for the practical application of electrocatalytic C-N coupling is designing high-performance catalysts to improve the energy efficiency, current density, and selectivity toward target products. To elucidate the mechanism of electrocatalytic C-N coupling, electrocatalysts with different structures, including size, morphologies, and components, should be designed to study the structure-activity relationships of catalytic sites and find how they influence the C-N coupling activity and selectivity. Advanced operando technologies with high resolution to monitor the key reaction intermediate and products are also crucial for determining the reaction pathway and capability. Meanwhile, a criterion should be devised for the electrocatalytic C-N coupling reactions, such as the essential data that ought to be presented in the paper: current density and their relative working potential, electrolyte parameters, feedstocks molar ratio optimization, etc. These will enable the readers to comprehend the reaction features of the respective reaction system and facilitate the determination of reaction mechanisms.

In addition, the industrial-level application needs high bias voltage to achieve an optimal current density, which will promote side reactions to decrease the FE of the target reaction. By using  $\text{CO}_2$  and  $\text{NO}_3^-$ , the main byproducts in the electrocatalytic C-N coupling process are CO,  $\text{NO}_2^-$ ,  $\text{H}_2$ ,  $\text{N}_2$ , and  $\text{NH}_3$ , requiring an additional product separation process. As mentioned in section 3.3, CO and  $\text{NH}_3$  byproducts could be used as feedstock for electrocatalytic amide synthesis in the formed industrial chain. For  $\text{NO}_2^-$ , it is crucial to consider improving the adsorption energy between  $^*\text{NO}_2$  and the catalyst surface to reduce its yield. For example, a single-atom Cu catalyst with a Cu-N-C structure alleviates the production of  $\text{NO}_2^-$ .<sup>65</sup> The combination of N and Cu atoms enhanced the adsorption energy between  $^*\text{NO}_2$  and the catalyst surface, thus inhibiting  $^*\text{NO}_2$  released to the aqueous solution.  $\text{N}_2$  and  $\text{H}_2$  could be easily removed from the aqueous solution without excess separation cost for other gaseous byproducts.

More importantly, suppressing side reactions is also essential. Minimizing the hydrogen evolution reaction (HER) competition benefits optimizing product components and reduces energy loss. The ideal catalyst should be able to reduce the adsorption of  $^*\text{H}$  on the active site, thus increasing the activation energy barrier of  $^*\text{H} \rightarrow \text{H}_2$ . Although employing an alkaline electrolyte is feasible to suppress HER in the electrocatalytic system, the active sites still dominate the reaction tendency. Unlike  $\text{H}_2$ , suppressing CO production requires the catalyst to adsorb  $^*\text{CO}$  on the active sites to realize the combinations during the C-N electrocatalytic coupling process. The design of multi-functional catalysts requires us to have a unique cognition of the in-depth mechanism, which needs theoretical studies to assist us in correcting the synthetic route of catalysts.

Theoretical studies, including machine learning (ML), density functional theory (DFT) simulations, and finite element simulations, also play an essential role in developing electrocatalytic C-N coupling technologies for recycling  $\text{CO}_2$  and N pollutants.<sup>66</sup> From the theoretical guidance, the structure-activity relationship of catalytic sites, the most suitable reaction pathways, and the local environment of catalytic interfaces could be investigated in depth. The ML technique is an ideal tool for catalyst modeling. With the help of ML methods, structures and contents of electrocatalysts could be fast screened, significantly improving the catalyst development efficiency and saving human resources in technology development. However, ML modeling still suffers from cost issues in accessing large, high-quality datasets. On the other hand, the reported catalytic models were based on their respective successes. In the current situation, ML can only be used as an additional tool, and the differences in application environments must be considered in practical applications.

Techno-economic analysis (TEA) should be a concern during the commercialization process (Figure 4, supplemental information). According to the proposed models, the catalyst cost, electrolyzer cost, separation cost, electricity cost, feedstock cost, maintenance cost, and operation cost were the basic manufacturing costs.<sup>27,67</sup> In scale-up applications, the overall energy economic efficiency mainly depends on energy consumption and technical efficiency. Specifically to C-N coupling electrocatalysis, the high-yield production and energy efficiency are beneficial to reduce the unit cost of production and separation. However, the selectivity of C-N coupling products in the existing studies is difficult to exceed 50% at the current stage. This will result in a significant increase in separation costs. The unsatisfactory selectivity of target products will significantly impact the separation cost and not be conducive to risk control of the practical applications. Therefore, improving the selectivity and yield of the target product for the catalyst is the top priority at the current stage. Also, it requires us to prioritize the large-scale synthesis of effective catalysts and the



**Figure 4.** Hypothetical schematic for the TEA of levelized cost of organonitrogen (based on the TEA method in the supplemental information)

improvement of large-scale electrocatalytic modules. With the development of renewable energy and separation methods, the actual cost will align with industrial and environmental expectations. Only when these goals are achieved, we can realize the industrial operation of C-N electrocatalytic coupling in the future decades.

In summary, while research to date on the C-N coupling process technology is insufficient to match the industrial demands, ongoing technical innovations promise to overcome limitations and enable practical applications. We believe it will provide new opportunities and insights for technological disruption in pollution control, electrocatalysis, and energy storage.

### SUPPLEMENTAL INFORMATION

Supplemental information can be found online at <https://doi.org/10.1016/j.isci.2023.107009>.

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### AUTHOR CONTRIBUTIONS

**Ye Ye:** Investigation, Writing. **Zhe Li:** Investigation, Visualization, Writing – original draft. **Shichao Ding:** Review & editing. **Jiaju Fu:** Review & editing, Resources – original draft. **Hongzhi Liu:** Review & editing. **Wenlei Zhu:** Conceptualization, Supervision, Writing – original draft.

### DECLARATION OF INTERESTS

The authors declare no conflict of interest.

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