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Catalysis for electrocatalytic C–N coupling towards amino acid synthesis

Xulin Nong,^a Chunqi Yang,^a Jingwen Zhuang,^a Yuhang Li ^{*a,b} and Chunzhong Li ^{*a,b,c}

Electrocatalytic amino acid synthesis, which uses renewable energy-generated electricity, can overcome the high energy consumption and environmental burden brought by classical methods. Here, we discuss the main steps of electrocatalytic amino acid synthesis and summarize the advanced progress in this field. The electrochemical processes are classified according to different nitrogen sources, namely NH_2OH , NO_3^- , NO , and NH_3 . Electrochemical synthesis can directly form C–N bonds under mild conditions through the reduction of nitrogen sources and the combination with carbon sources. However, when nitrogen oxides are used as nitrogen sources, excessive reduction to ammonia can reduce the selectivity of amino acids. Therefore, the rational design of catalysts is crucial to balance the kinetic mismatch and intermediate stability to achieve selective amino acid production. Finally, we provide an outlook on performance improvement strategies for electrochemical amino acid synthesis to encourage further research efforts and development in this field.

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1. Electrocatalytic synthesis is a green alternative method for producing amino acids. It employs renewable electricity under mild conditions to form C–N bonds from accessible feedstocks such as CO_2 , nitrate or nitric oxide, and biomass-derived α -keto acids, avoiding the use of toxic cyanides and energy-intensive classical methods.
2. The significance of this area lies in its potential to convert wastes into valuable products, contribute to carbon neutrality aims, and provide a flexible route for producing amino acids and related fine chemicals.
3. Future development depends on improving catalyst design, deepening mechanistic understanding through *in situ* analysis, and advancing reactor engineering such as membrane electrode assemblies. The insights offered aim to support the design of more efficient and circular electrochemical processes, aiding progress toward a more sustainable chemical industry.

1. Introduction

As essential building blocks of life, amino acids are utilized in medicine,¹ food production,² and agriculture.³ Industrial amino acid synthesis methods, including extraction, chemical synthesis, and biological fermentation, face challenges such as high energy consumption, reliance on toxic reagents, multi-step processes, and environmental burdens. For example, the Strecker synthesis requires high temperature and pressure conditions and has low atom economy,⁴ while biological approaches are limited by enzyme stability and substrate

specificity.^{5,6} With the urgency of achieving global carbon neutrality, developing efficient and sustainable pathways for amino acid synthesis has become a key research field.

The electrochemical synthesis method presents a promising green alternative for amino acid manufacturing, owing to its utilization of clean energy and operation under mild reaction conditions. This technology centers on the coupling reaction of electrochemical reduction of nitrogen sources (NO_x , NH_3) with carbon sources (α -keto acids, CO_2 derivatives) to construct C–N bonds and complete the hydrogenation process. For example, using nitrates from industrial wastewater or NO from waste gas as nitrogen sources, combined with biomass-derived α -keto acids or CO_2 reduction products (such as oxalic acid), efficient synthesis of amino acids can be achieved at room temperature and pressure. Such methods not only upgrade waste into high-value-added products but also avoid the use of toxic reagents like cyanides in conventional processes and are conducive to the goal of carbon neutrality.

The electrocatalytic synthesis of amino acids involves three key steps: (1) the reduction of nitrogen sources to generate

^aKey Laboratory for Ultrafine Materials of Ministry of Education, Shanghai Engineering Research Center of Hierarchical Nanomaterials, School of Materials Science and Engineering, East China University of Science and Technology, Shanghai 200237, China. E-mail: yuhangli@ecust.edu.cn, czli@ecust.edu.cn

^bDepartment of Chemical Engineering, School of Chemistry and Chemical Engineering, Shanghai Jiao Tong University, Shanghai 200240, China

^cSchool of Chemical Engineering, East China University of Science and Technology, Shanghai 200237, China

reactive nitrogen intermediates (hydroxylamine NH_2OH , NH_3), (2) the condensation of intermediates with carbon sources to form oximes or imines, and (3) further hydrogenation to produce the target amino acids. Among these, hydroxylamine, due to its unique nucleophilicity and reducing properties, becomes the core intermediate in the cascade reaction. However, electrochemical synthesis still faces multiple challenges: (1) the synchronous adsorption and reduction kinetics of nitrogen and carbon sources are mismatched, leading to intense competition from a side reaction, the hydrogen evolution reaction (HER); (2) oximes exhibit low stability and undergo non-selective decomposition; and (3) designing catalysts for complex multi-step pathways requires synergistic active sites, imposing stringent demands on precise control of material structures and electronic states.

Following the 2019 pioneering work of Takashi Fukushima and Miho Yamauchi⁷ on electrochemical amino acid synthesis from α -keto acids and NH_2OH , research in this field has expanded significantly. Innovations in catalyst engineering and reactor design have significantly advanced the field. Bimetallic catalysts^{8,9} optimize nitrogen reduction and carbon hydrogenation steps through spatial site isolation,¹⁰ markedly improving faradaic efficiency for glycine synthesis. Atomically dispersed catalysts^{11,12} enhance product selectivity by lowering further hydrogenation energy barriers.¹³ Reactor optimizations, such as spatially decoupled dual-reactor systems,¹⁴ enhance synthesis efficiency by segregating intermediate generation and conversion steps. Despite these advancements, understanding of reaction mechanisms across diverse nitrogen sources and cascade reaction design remains limited. Furthermore, the dynamic interplay between C–N bond formation and catalyst structural evolution requires deeper exploration.

This review aims to summarize the latest advances in electrocatalytic amino acid synthesis. We first outline the reaction pathways and mechanistic frameworks of electrocatalytic synthesis. Next, we categorize key breakthroughs based on nitrogen sources, providing the key research achievements and technological breakthroughs in this field. Finally, in view of the core challenges existing in the current research, the key directions for future development are proposed around aspects such as catalyst design optimization, reaction pathway innovation, and the construction of a standardized evaluation system, with the expectation of providing theoretical support and practical reference for in-depth exploration and industrial application in this field.

2. Electrochemical amino acid synthesis

2.1. Pathway and mechanism

The core of electrocatalytic amino acid synthesis involves the spontaneous condensation of nitrogen precursors with carbon sources to form C–N bonds, followed by hydrogenation to construct the amino acid structures. Oxalic acid and α -keto acids

serve as critical carbon sources for the electrochemical synthesis of amino acids. Oxalic acid production routes include electrocatalytic oxidation of ethylene glycol (a hydrolysis by-product of PET plastics)^{15,16} and CO_2 electroreduction.^{17–19} Nitrogen sources including NO and NO_3^- are obtained from industrial wastewater and exhaust gas. This methodological approach integrates waste-derived reagents, including plastic waste, carbon dioxide, and industrial byproducts, into a cohesive catalytic cycle. This integration facilitates C–N bond formation under ambient conditions and reduces toxic intermediate generation.

Electrocatalytic amino acid synthesis proceeds in three steps. First, nitrogen sources (e.g., NO_3^- , NO) are reduced to NH_2OH or NH_3 on the catalyst surface. Next, nucleophilic addition or condensation with carbon sources (typically α -keto acids) forms oxime or imine intermediates. Finally, intermediates are further hydrogenated to form the target amino acids. The reaction process involves sequential intermediates: hydroxylamine, oxime, and imine species. In electrocatalytic amino acid synthesis, non-hydroxylamine nitrogen sources first convert into hydroxylamine intermediates, which then undergo nucleophilic addition with carbon precursors to generate oxime species. Subsequent reduction of oximes produces imines, while ammonia skips oxime formation entirely, directly condensing with carbon precursors to form imines,^{7,20} ultimately yielding amino acids (Fig. 1).

In the electrocatalytic amino acid synthesis system, major side reactions such as excessive hydrogenation of NO_3^- to produce NH_3 , the hydrogen evolution reaction (HER), and non-selective hydrogenation of α -keto acids/aldehyde acids seriously limit the system's selectivity and industrial potential. These side reactions not only compete with the target reaction for electrons and protons, consuming key intermediates, which markedly reduce the faradaic efficiency and yield of amino acids, but also increase the difficulty and energy consumption of downstream product separation and purification. The fundamental cause lies in the kinetic imbalance in multi-step tandem reactions and the imprecise regulation of the catalyst's adsorption energy for critical intermediates, which must be addressed through catalyst design and reactor improvement to suppress these side reactions.

2.2. Compared with industrial synthesis of amino acids

Contemporary global amino acid manufacturing primarily relies on extraction techniques, chemical synthesis, and biological processes. Electrocatalytic synthesis emerges as a transformative approach with several distinct advantages. Environmentally sustainable operation avoids toxic reagents (e.g., cyanides) and high-energy inputs from conventional chemical synthesis,^{4,21} and reduces CO_2 emissions to support carbon neutrality goals. This method achieves superior atom economy through voltage-modulated selective bond activation, enabling near-quantitative utilization of precursors during CO_2 electroreduction coupled with hydroxylamine, contrasting with the multi-step hydrolysis inherent in Strecker synthesis.¹⁴ Mild ambient conditions eliminate the need for pressurized

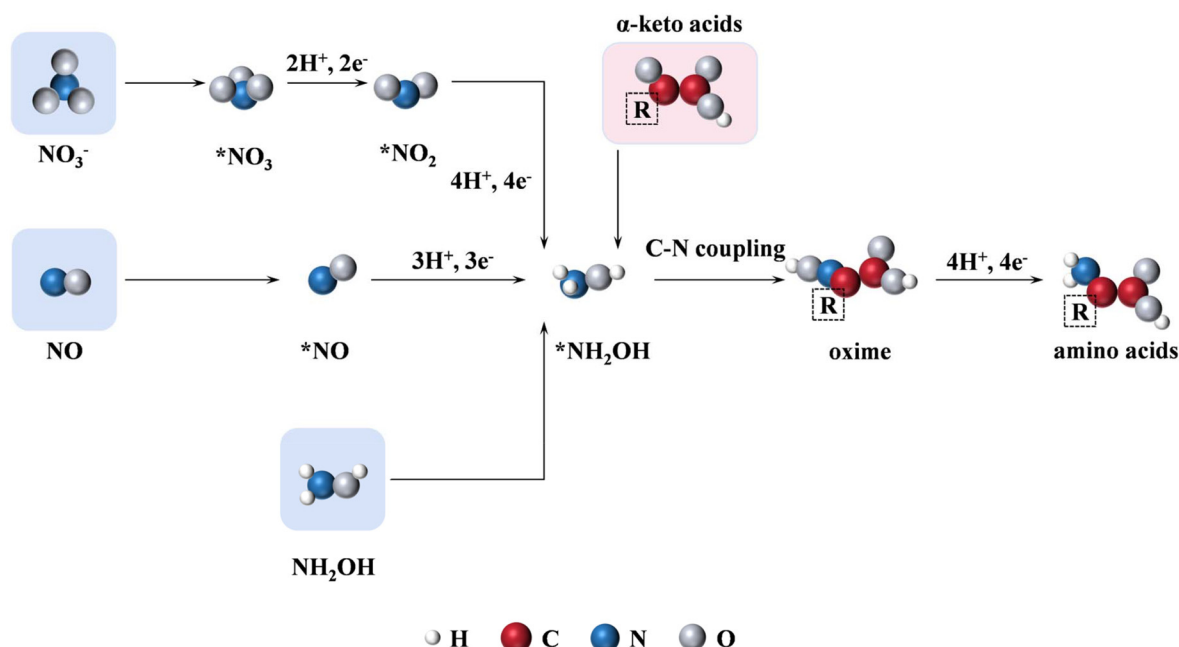


Fig. 1 Schematic representation of electrocatalytic synthesis of amino acids from different nitrogen sources.

reactors or stringent oxygenation controls,^{5,21} instead employing simplified electrolyser configurations with stable current inputs. The catalytic process is streamlined by avoiding immobilized enzymes and streamlining catalyst recovery, while modular electrolyser arrays enable flexible capacity adjustments for specialized products such as non-canonical amino acids. Electrochemical parameter tuning (precursor selection, potential modulation) facilitates the synthesis of structurally complex variants, including D-enantiomers and fluorinated analogs, with precise stereochemical control achieved through chiral electrodes to ensure pharmaceutical-grade optical purity.²² This integrated platform combines operational simplicity with product diversification capabilities, addressing critical limitations of classical manufacturing paradigms.

Given these advancements, electrocatalytic synthesis shows potential to revolutionize amino acid manufacturing. Realizing this potential requires replacing laboratory demonstrations with industrial-scale assessment for practical validation. Large-scale application further requires quantitative assessment of economic and environmental metrics *via* technical and economic analysis (TEA) and life cycle assessment (LCA).²³ These two tools will provide a crucial decision-making basis for process optimization and industrialization direction.

The core dimensions of TEA: (1) raw material costs. The acquisition and purification costs of nitrogen sources (industrial wastewater (NO_3^-), exhaust gas (NO), or commercial ammonia (NH_3)) need to be classified and accounted for. Wastewater/exhaust gas treatment incurs additional processing costs. Commercial ammonia, though available, faces limitations due to energy-intensive production. Carbon source costs require full evaluation of material collection, conversion

efficiency, and separation energy consumption. (2) Energy input. Electricity is the main driving force, but low faradaic efficiency leads to a significant loss of electricity in the side reaction. The cost of product separation consumes additional heat/mechanical energy, and its cost increases exponentially with the decrease in product concentration. The current economic concentration threshold of the electrochemical synthesis system lacks a clear definition and requires optimization using quantitative methods through TEA. (3) Comprehensive cost. The synthesis and regeneration costs of catalysts and the capital expenditure and maintenance costs of modular electrolyzers. The key issues of LCA: (1) environmental benefits. Carbon footprint reduction: utilizing waste nitrogen sources NO_x and CO_2 can reduce greenhouse gas emissions compared to the Strecker synthesis method. Toxicity control: avoiding toxic reagents, such as cyanide, reduces the ecological toxicity load of water bodies. (2) Potential environmental impacts. Energy structure: it is necessary to distinguish the differences in LCA between scenarios driven by renewable energy and grid power supply.

By-products management: the NH_3 or metal leaching substances (such as Bi^{3+}) generated during the reaction need to be included in the impact accounting. (3) Environmental benefit comparison of process paths: the environmental benefit of *in situ* electrochemical synthesis of NH_2OH is superior to that of purchased NH_2OH .

To more objectively evaluate the industrial feasibility of different electrocatalytic synthesis systems, we further emphasize from a techno-economic analysis perspective that faradaic efficiency (FE), partial current density, and product yield rate are core indicators for assessing the practical application value

of a system: high FE is directly related to energy consumption costs, high partial current density determines reactor scale and capital expenditure, and high product yield rate reflects material utilization efficiency and process economics.

3. Different nitrogen sources for synthesizing amino acids

This chapter will present the strategies and research progress of electrocatalytic amino acid synthesis based on different nitrogen sources. It will focus on the innovative catalyst design corresponding to various nitrogen sources, optimization of reaction pathways, and understanding of reaction mechanisms. Through an in-depth analysis of the performance of different catalytic systems (such as single-atom catalysts, bimetallic/multimetallic catalysts, carbon-based materials, *etc.*) in the conversion of specific nitrogen sources and C–N coupling, this chapter aims to clarify the structure–activity relationship between the catalyst structure, active sites, and synthesis efficiency/selectivity. Table 1 summarizes and compares the key electrochemical synthesis performance parameters based on different nitrogen sources (such as faradaic efficiency, yield, reactor type, and stability), providing an intuitive reference for assessing the current status and potential of different technological routes.

The selection of a nitrogen source profoundly influences the reaction pathway, catalyst design, and ultimately the economic viability of electrocatalytic amino acid synthesis. A comparative analysis of the common nitrogen sources reveals their distinct characteristics: the NH_2OH -based system offers the highest selectivity and the clearest reaction mechanism, yet it suffers from high raw material costs and potential safety risks. The NO_3^- -based system, with its wide availability from waste streams (*e.g.*, industrial wastewater), presents significant advantages for resource utilization and is currently considered the most promising nitrogen source for industrialization. The NO -based system typically exhibits fast reaction rates but is often accompanied by side reactions, necessitating structured reactor designs (*e.g.*, flow cells) for effective scaling. The NH_3 -based system features the most straightforward reaction steps; however, the high energy barrier for C–N coupling requires catalysts with special structures, such as certain metals or carbon-based materials. Comprehensive analysis indicates that the reaction pathway of “nitrate + α -keto acid”, coupled with the membrane electrode assembly (MEA) reactor design, is recognized as the most promising reaction mode at present.

3.1. NH_2OH as the nitrogen source

Hydroxylamine (NH_2OH) has emerged as a key nitrogen source and intermediate in the electrocatalytic synthesis of amino acids due to its unique reductive and nucleophilic properties for C–N bond formation. Fukushima and his colleagues⁷ have electrocatalytically synthesized seven amino acids (such as alanine, glycine, aspartic acid, glutamic acid, *etc.*) using biomass-derived α -keto acids and NH_2OH as raw materials,

based on the theory of reductive amination, combining electrochemical drive and the high selectivity of TiO_2 catalysts for the reduction of carbonyl compounds in aqueous media. In an acidic medium, the spontaneous condensation between NH_2OH and α -keto acids yields oxime intermediates ($\text{R}-\text{C}=\text{N}-\text{OH}$), followed by their electroreduction to amino acids. A flow-type electrochemical reactor “Polymer electrolyte amino acid electro-synthesis cell” achieved continuous alanine production with 77% faradaic efficiency (Fig. 2b and c). The team further expanded the range of substrates by investigating the feasibility of glycine synthesis through single-step reduction, utilizing oxalic acid as the precursor.²⁴ Results revealed that calcined Ti foil (450 °C) catalyzes the gradual reduction of oxalic acid to glyoxal oxime at -0.7 V vs. RHE , followed by reduction to glycine, with a total FE of 56%. This work focuses on catalyst optimization (including the screening of materials such as Mo, Ti, *etc.*) and improves the reaction conditions to enhance selectivity and yield. At the same time, carbon dioxide derivatives have potential as carbon sources for amino acid synthesis.

Catalyst engineering significantly enhances selectivity. Li *et al.*²⁵ have prepared a Pb–Cu dual-site catalyst, where the Pb site facilitated selective reduction of oxalic acid to glyoxylic acid, and the Cu site accelerated oxime hydrogenation to glycine. At an industrial current density of 200 mA cm^{-2} , the FE of glycine reached 78% (Fig. 2d), and it was coupled with the oxidation of formaldehyde (FOR) to reduce energy consumption. *In situ* ATR-FTIR revealed the tandem reaction pathway and verified the dual-site synergy mechanism (Fig. 2e). Through the spatial separation of catalyst sites, the selectivity challenge in complex reaction pathways was solved, promoting the electrochemical synthesis technology to industrialization. In a different study,²⁶ researchers have designed a $\text{CuPb}_{1\text{ML}}$ electrode through underpotential deposition of Pb for the electrocatalytic synthesis of glycine. The study showed that only a monolayer of Pb was sufficient to suppress the hydrogen evolution reaction (HER) and increase the FE of glycine. Compared with pure Pb and Cu electrodes, the $\text{CuPb}_{1\text{ML}}$ electrode exhibited higher FE 57% and catalytic activity ($211\text{ }\mu\text{mol h}^{-1}\text{ cm}^{-2}$) in glycine production. *In situ* FTIR spectroscopy (Fig. 2f) and surface analysis clarified that the Pb monolayer redistributed to form particles during the catalytic process, exposing part of the Cu surface, while the Cu surface was passivated through Pb surface alloying, thereby inhibiting the HER. Shi and his team²⁷ have proposed bimetallic Ag/Cu nanowires (NWs) that achieved effective catalysis for the electroreduction amination of α -keto acids to α -amino acids by adjusting the adsorption geometry and reconstructing the electronic structure. This catalyst reduced the reaction onset potential and improved the amino acid yield. The mechanism explained by density functional theory (DFT) calculations indicates that the addition of Ag modifies the adsorption geometry of the reaction intermediates, facilitates the transfer of electrons from Cu to Ag, optimizes the electronic structure of the catalyst, and further lowers the energy barrier of the rate-determining

Table 1 Summary of the electrochemical synthesis performance of amino acids by diverse nitrogen sources

N source	Electrocatalyst	Electrolyte	Voltage	Yield rate	FE _{amino acid}	Reactor	Stability	Ref.
NH ₂ OH	TiO ₂ /Ti Ti foil ed-PbCu CuPb _{IML} Ag/Cu NWs	0.2 M H ₂ SO ₄ + 0.16 M PA + 0.096 M (NH ₂ OH) ₂ ·H ₂ SO ₄	−2.4 V	0.430 mmol h ^{−1} cm ^{−2}	77.0% (Ala)	Flow cell	1.66 h	7
		0.5 M H ₂ SO ₄ + 0.16 M OA + 0.096 M (NH ₂ OH) ₂ ·H ₂ SO ₄	−0.7 V _{RHE}	0.007 mmol h ^{−1} cm ^{−2}	28.0% (Gly)	H cell	2 h	24
		0.1 M K ₂ SO ₄ + 0.2 M H ₂ SO ₄ + 0.25 M OA + 0.25 M NH ₂ OH	0.6–1.2 V	0.970 mmol h ^{−1} cm ^{−2}	78.0% (Gly)	MEA	55 h	25
		0.1 M H ₂ SO ₄ + 0.25 M OA + 0.25 M NH ₂ OH	−1.3 V _{RHE}	0.211 mmol h ^{−1} cm ^{−2}	57.0% (Gly)	H cell	48 h	26
		0.2 M H ₂ SO ₄ + 0.16 M PA + 0.096 M (NH ₂ OH) ₂ ·H ₂ SO ₄	−0.32 V _{RHE}	0.690 mmol h ^{−1} cm ^{−2}	85.3% (Ala)	H cell	25 h	27
		0.2 M H ₂ SO ₄ + 0.16 M keto acid + 0.096 M (NH ₂ OH) ₂ ·H ₂ SO ₄	−0.32 V _{RHE}	1.120 mmol h ^{−1} cm ^{−2}	76.9% (Gly)			
			−0.32 V _{RHE}	0.640 mmol h ^{−1} cm ^{−2}	82.3% (Asp)			
			−0.32 V _{RHE}	0.621 mmol h ^{−1} cm ^{−2}	70.5% (Glu)			
			−0.32 V _{RHE}	0.575 mmol h ^{−1} cm ^{−2}	87.0% (Leu)			
			−0.6 V _{RHE}	1.040 mmol h ^{−1} cm ^{−2}	85.1% (Gly)	H cell	160 h	28
			2.7 V	0.835 mmol h ^{−1} cm ^{−2}	87.0% (Phe)	Flow cell	—	29
			−0.01 V _{RHE}	—	89.0% (Glu)	H cell	2.5 h	30
	Cu foam@Cu NPs Ti foil Nanoporous gold	0.5 M H ₂ SO ₄ + 0.2 M GA + 0.1 M NH ₂ OH	−0.01 V _{RHE}	—	74.0% (Gly)			
		0.1 M LiClO ₄ MeCN/H ₂ O (v/v: 2/1) + 0.02 M DL-mandelic acid + 0.03 M NH ₂ OH	−0.01 V _{RHE}	—	89.0% (Leu)			
		0.15 M NaCl + 0.05 M α-keto acid + 0.05 M NH ₂ OH (pH = 1.6)	−0.01 V _{RHE}	—	93.0% (Ala)			
			−0.01 V _{RHE}	—	91.0% (Asp)			
		0.5 M H ₂ SO ₄ + 0.15 M PA + 0.15 M NH ₂ OH	2.0 V	0.112 mmol h ^{−1} cm ^{−2}	75.0% (Ala)	Flow cell	—	31
		0.5 M H ₂ SO ₄ + 0.15 M GA + 0.18 M NH ₂ OH	−0.32 V _{RHE}	0.186 mmol h ^{−1} cm ^{−2}	84.0% (Gly)	MEA	27.5 h	32
		0.2 M Na ₂ SO ₄ + 0.08 M PA + 0.096 M NH ₂ OH	−0.62 V _{RHE}	0.162 mmol h ^{−1} cm ^{−2}	90.5% (Ala)	H cell	2 h	33
		0.2 M Na ₂ SO ₄ + 0.08 M substrate + 0.096 M NH ₂ OH	−0.62 V _{RHE}	0.122 mmol h ^{−1} cm ^{−2}	74.1% (Gly)			
			−0.62 V _{RHE}	0.097 mmol h ^{−1} cm ^{−2}	69.8% (Val)			
			−0.62 V _{RHE}	0.092 mmol h ^{−1} cm ^{−2}	64.8% (Leu)			
			−0.62 V _{RHE}	0.124 mmol h ^{−1} cm ^{−2}	65.8% (Asp)			
			−0.62 V _{RHE}	0.087 mmol h ^{−1} cm ^{−2}	51.3% (Glu)			
NO ₃ [−]	Ag-foam PdCu NBWs Fe–N–C-700 adFe–TiO ₂ /Ti F–Cu ₃ –OF	0.2 M H ₂ SO ₄ + 0.16 M GA + 0.08 M (NH ₂ OH) ₂ ·H ₂ SO ₄	—	0.706 mmol h ^{−1} cm ^{−2}	— (Gly)	H cell	20 h	34
		0.2 M H ₂ SO ₄ + 0.16 M PA + 0.08 M (NH ₂ OH) ₂ ·H ₂ SO ₄	—	0.582 mmol h ^{−1} cm ^{−2}	— (Ala)	H cell	2.5 h	
		0.2 M H ₂ SO ₄ + 0.16 M α-ketoglutaric acid + 0.08 M (NH ₂ OH) ₂ ·H ₂ SO ₄	—	0.478 mmol h ^{−1} cm ^{−2}	— (Glu)	H cell	3 h	
		1 M KOH + 0.2 M KH ₂ PO ₄ + 50 mM PA + 1.0 M KNO ₃	−0.3 V _{RHE}	—	— (Ala)	H cell	—	10
		1 M KOH + 0.2 M KH ₂ PO ₄ + 100 mM PA + 2.0 M KNO ₃	1.7 V	0.400 mmol h ^{−1} cm ^{−2}	— (Ala)	Flow cell	48 h	
		0.5 M OA + 0.5 M NaNO ₃	−0.9 V _{RHE}	0.331 mmol h ^{−1} cm ^{−2}	64.2% (Gly)	H cell	15 h	13
		0.5 M H ₂ SO ₄ + 0.1 M GA + 1.0 M NaNO ₃	−0.7 V _{RHE}	0.236 mmol h ^{−1} cm ^{−2}	31.0% (Gly)	H cell	—	35
			2.07–2.19 V	0.214 mmol h ^{−1} cm ^{−2}	— (Gly)	Flow cell	100 h	
			−0.6 V _{RHE}	0.957 mmol h ^{−1} cm ^{−2}	71% (Ala)	Flow cell	24 h	36
			−0.6 V _{RHE}	0.354 mmol h ^{−1} cm ^{−2}	42% (Gly)			
			−0.6 V _{RHE}	0.300 mmol h ^{−1} cm ^{−2}	66% (Val)			
			−0.6 V _{RHE}	0.187 mmol h ^{−1} cm ^{−2}	57% (Leu)			
	PbSnBi Cu/Bi–C@CF Cu–Hg CoPc/CNT	0.5 M KOH + 0.2 M PA + 0.2 M NO ₃ [−]	−0.6 V _{RHE}	0.515 mmol h ^{−1} cm ^{−2}	55% (Phe)			
		1.5 M H ₂ SO ₄ + 0.25 M OA + 0.25 M NO ₃ [−]	−1.5 V _{SCE}	1.125 mmol h ^{−1} cm ^{−2}	57.2% (Gly)	H cell	20 h	37
		0.1 M HCl + 20 mM GA + 300 mM NO ₃ [−]	−0.65 V _{RHE}	0.050 mmol h ^{−1} cm ^{−2}	65.9% (Gly)	H cell	105 h	38
		15 wt% H ₂ SO ₄ + 0.25 M OA + 0.25 M NaNO ₃	−1.4 V _{Ag/Ag} ⁺	0.121 mmol h ^{−1} cm ^{−2}	43.1% (Gly)	H cell	10.5 h	39
		0.4 M H ₂ SO ₄ + 0.2 M PA + 1 M KNO ₃	−0.57 V _{RHE}	0.096 mmol h ^{−1} cm ^{−2}	61.2% (Ala)	H cell	1.11 h	40
			−0.59 V _{RHE}	0.076 mmol h ^{−1} cm ^{−2}	60.4% (Glu)			
			−0.59 V _{RHE}	0.053 mmol h ^{−1} cm ^{−2}	47.0% (Gly)			
			−0.55 V _{RHE}	0.018 mmol h ^{−1} cm ^{−2}	26.7% (Leu)			
			−0.60 V _{RHE}	0.005 mmol h ^{−1} cm ^{−2}	14.2% (Val)			
			—	0.159 mmol h ^{−1} cm ^{−2}	42.8% (Gly)	H cell	60 h	41
			−0.5 V _{RHE}	0.093 mmol h ^{−1} cm ^{−2}	49.3% (Gly)	H cell	2 h	42
			−0.5 V _{RHE}	0.048 mmol h ^{−1} cm ^{−2}	38.2% (Ala)			
			−0.5 V _{RHE}	0.028 mmol h ^{−1} cm ^{−2}	17.5% (Asp)			
NO	TiO ₂ /CNT-1000 Pb ₂ Bi _{0.1}	0.2 M HClO ₄ + 0.05 M OA + 0.05 M HNO ₃	−0.5 V _{RHE}	0.019 mmol h ^{−1} cm ^{−2}	13.0% (Leu)			
		1.5 M H ₂ SO ₄ + 0.25 M PA + 0.25 M NaNO ₃	−0.84 V _{Ag/Ag} ⁺	—	57.0% (Gly)	H cell	—	43
		1.5 M H ₂ SO ₄ + α-keto acid + 0.25 M NaNO ₃	−1.5 V _{SCE}	1.245 mmol h ^{−1} cm ^{−2}	59.7% (Ala)	H cell	24 h	44
			−1.5 V _{SCE}	1.070 mmol h ^{−1} cm ^{−2}	52.6% (Phe)			
			−1.5 V _{SCE}	0.625 mmol h ^{−1} cm ^{−2}	46.1% (Gly)			
			−1.5 V _{SCE}	0.775 mmol h ^{−1} cm ^{−2}	36.4% (Asp)			
			−1.5 V _{SCE}	0.337 mmol h ^{−1} cm ^{−2}	25.3% (Leu)			
			−1.5 V _{SCE}	0.392 mmol h ^{−1} cm ^{−2}	20.9% (Val)			
			−1.5 V _{SCE}	0.587 mmol h ^{−1} cm ^{−2}	20.6% (Glu)			
			−0.76 V _{RHE}	0.556 mmol h ^{−1} cm ^{−2}	79.1% (Gly)	H cell	40 h	45
			−0.76 V _{RHE}	0.099 mmol h ^{−1} cm ^{−2}	51.9% (Ala)			
			−0.76 V _{RHE}	0.062 mmol h ^{−1} cm ^{−2}	38.3% (Leu)			
	e-Bi Cu/Cu ₂ O	0.05 M KH ₂ PO ₄ + 0.5 M KOH + 0.2 M PA + 0.5 M KNO ₃	−0.6 to −0.7 V _{RHE}	0.239 mmol h ^{−1} cm ^{−2}	75.8% (Ala)	H cell	30 h	46
			−0.4 V _{RHE}	0.134 mmol h ^{−1} cm ^{−2}	51.2% (Glu)			
			−0.2 V _{RHE}	0.049 mmol h ^{−1} cm ^{−2}	46.0% (Gly)			
			−0.4 V _{RHE}	0.022 mmol h ^{−1} cm ^{−2}	21.5% (Leu)			
			−0.56 V _{RHE}	0.023 mmol h ^{−1} cm ^{−2}	17% (Ala)	H cell	5 h	14
			3.0–4.5 V	—	70% (Ala)	Flow cell	120 h	
			—	0.222 mmol h ^{−1} cm ^{−2}	79.1% (Gly)	H cell	120 h	41
			−0.7 V _{RHE}	0.029 mmol h ^{−1} cm ^{−2}	32.4% (Leu)	H cell	240 h	47
			−0.6 V _{RHE}	0.005 mmol h ^{−1} cm ^{−2}	— (Val)	H cell	19 h	48
			−0.39 V _{RHE}	0.181 mmol h ^{−1} cm ^{−2}	90.0% (Glu)	H cell	8 h	20
			−0.39 V _{RHE}	0.017 mmol h ^{−1} cm ^{−2}	87.4% (Gly)	H cell	—	
			−0.39 V _{RHE}	0.043 mmol h ^{−1} cm ^{−2}	45.0% (Ala)			
	BM3h–CNTs	100 mM GA + 6 M NH ₄ OH	−0.39 V _{RHE}	0.015 mmol h ^{−1} cm ^{−2}	46.9% (Asp)			
		60 mM substrate + 6 M NH ₄ OH	−0.39 V _{RHE}	—	1.2% (Ser)	H cell	24 h	22
NH ₃	Cu(I–CCFs)	0.25 M NH ₄ HCO ₃	−0.6 to −1.3 V _{RHE}	—	—			

PA: pyruvic acid C₃H₄O₃, GA: glyoxylic acid C₂H₂O₃, OA: oxalic acid H₂C₂O₄, Gly: glycine C₂H₅NO₂, Ala: alanine C₃H₇NO₂, Phe: phenylalanine C₉H₁₁NO₂, Glu: glutamic acid C₅H₉NO₄, Leu: leucine C₆H₁₃NO₂, Ser: serine C₃H₇NO₃, Val: valine C₅H₁₁NO₂.

step of the reaction (Fig. 2g and h). In addition, the catalyst was applicable to the synthesis of various α-amino acids, supporting the key role of bimetallic systems and reactor design in enhancing the efficiency of electrocatalytic synthesis.

Reaction pathway engineering offers additional selectivity control. Kong *et al.*²⁸ have proposed a three-step cascade strategy. CO₂ is first reduced to oxalic acid (H₂C₂O₄) *via* electrocatalysis, which is then further reduced to glycolic acid (C₂H₂O₃). Meanwhile, NH₂OH is synthesized by lithium-mediated N₂ fix-

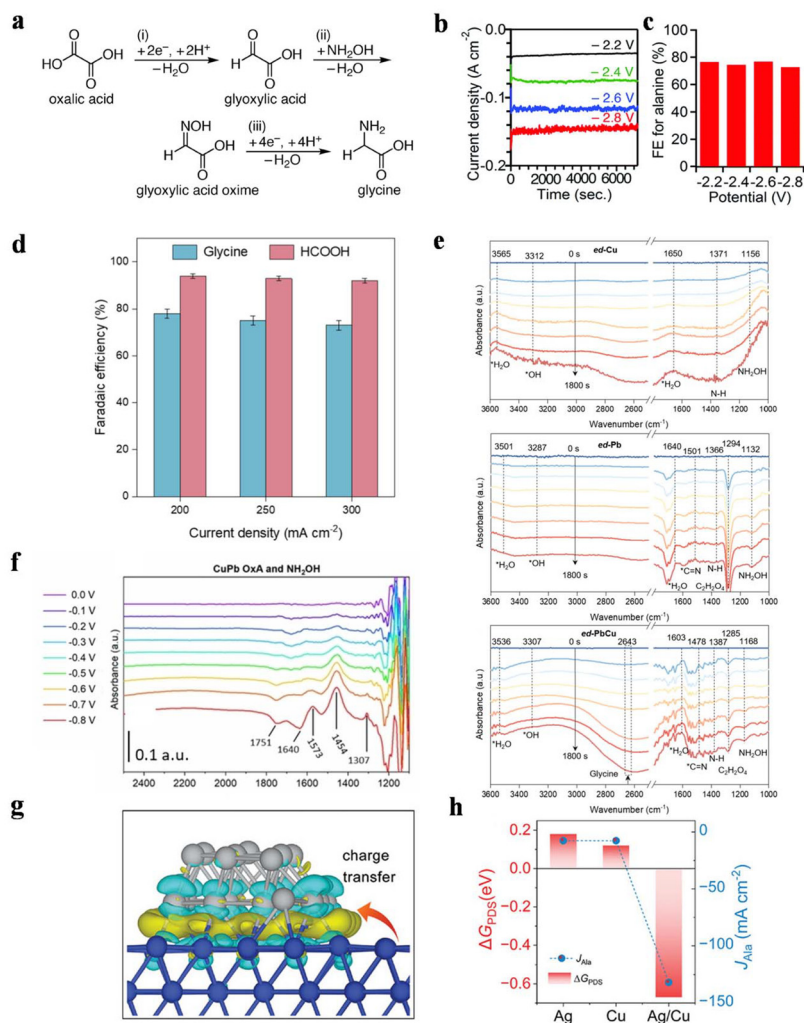


Fig. 2 (a) Reaction path for producing glycine from oxalic acid, adapted from ref. 24 with permission from Springer Nature, copyright 2020. (b) The current density at various application potentials within the range of 2.2 to 2.8 V during the operation of the AAEC, as well as (c) FE for the production of alanine, adapted from ref. 7 with permission from the Royal Society of Chemistry, copyright 2019. (d) Partial faradaic efficiency of cathodic glycine and anodic HCOOH at different current densities; (e) time-dependent electrochemical *in situ* ATR-FTIR spectra of the ed-Cu, ed-Pb, and ed-PbCu using $\text{H}_2\text{C}_2\text{O}_4$ and NH_2OH as reactants, adapted from ref. 25 with permission from American Chemical Society, copyright 2024. (f) FTIR spectra at different potentials vs. RHE for the CuPb_{1ML} electrode with 0.25 M oxalic acid and 0.25 M NH_2OH in aqueous 0.1 M H_2SO_4 , adapted from ref. 26 with permission from Wiley-VCH, copyright 2023. (g) The Bader charge transfer and charge density difference for the Ag(111)/Cu(111) composite catalyst. (h) The ΔG_{PDS} and partial current density of alanine on Ag, Cu, and Ag/Cu catalysts, adapted from ref. 27 with permission from Wiley-VCH, copyright 2025.

ation and the reduction of O_2 to H_2O_2 . Ultimately, glyoxylic acid and NH_2OH undergo a condensation reaction to form glyoxylic acid oxime ($\text{C}_2\text{H}_3\text{NO}_3$), which is further reduced to obtain high-purity glycine solid powder. This process achieves a green and sustainable synthesis from air components to amino acids, with a carbon selectivity from CO_2 to glycine reaching 91.7% and a nitrogen selectivity from N_2 to glycine reaching 98.7%. They also designed a three-dimensional Cu catalyst (Cu foam@Cu NPs) to enhance the catalytic activity for the electroreduction of $\text{C}_2\text{H}_3\text{NO}_3$. The partial current density of glycine reached 160.8 mA cm^{-2} , with stability up to 160 h. DFT calculations revealed the advantages of Cu as a catalyst in the electroreduction of glyoxylic acid oxime to glycine. The

adsorption energy of glyoxylic acid oxime on the Cu surface is moderate, ensuring the effective adsorption of substrates while avoiding catalyst poisoning due to excessive adsorption. The hydrogen adsorption energy on the Cu surface is within an ideal range, making the proton-involved reaction step the rate-determining step and achieving efficient electrocatalytic conversion.

3.2. Other nitrogen sources

3.2.1. NO_3^- as the nitrogen source. In the process of electrocatalytic synthesis of amino acids, the design of the catalyst is of vital importance. The ideal catalyst needs to have both efficient nitrogen reduction and carbon reduction

capabilities and be able to promote the formation of C–N bonds. Zhou *et al.*⁴⁰ have developed a composite catalyst (CoPc/CNT) based on cobalt phthalocyanine (CoPc) and carbon nanotubes (CNTs). Through the synergistic effect of CoPc molecules and CNTs, nitrate undergoes efficient reduction to NH_2OH , followed by a C–N coupling reaction with α -keto acid to generate amino acids such as alanine, glutamic acid, and glycine. The experimental results show that at the potential of -0.57 V vs. RHE, the faradaic efficiency of alanine of this catalyst is as high as 61%, and the partial current density reaches 42 mA cm^{-2} . Furthermore, Xian *et al.*⁴¹ designed a Co nanoparticle (Co–HCNF) encapsulated in hollow carbon nanofibers for the synthesis of amino acids from ketone acids derived from waste NO_x and biomass. With its unique mesoporous structure, it provides abundant active sites. When NO_3^- is used as the nitrogen source, the FE of glycine is 42.8%, the yield is as high as $159.5\text{ }\mu\text{mol h}^{-1}$, and it shows stability for up to 60 hours.

Single-atom catalysts can alter the adsorption/desorption selectivity of the active components on the catalyst surface for different molecules, thereby influencing the reaction kinetics. Cheng *et al.*¹³ have reported an electrochemical strategy that employs an Fe–N–C catalyst with atomic dispersion to mediate the reductive coupling of oxalic acid with nitrate or nitrogen oxides, leading to glycine. The catalyst achieved a glycine selectivity of 70.7% under the condition of -1.0 V vs. RHE. The research demonstrated that the catalytic synergy arising from the interaction between the FeN_3C moiety and adjacent nitrogen active sites significantly enhanced the selective hydrogenation of oxalic acid to glyoxylic acid (GX). This transformation serves as a pivotal intermediate step in the subsequent synthesis of glyoxylic acid oxime and glycine. In addition, the FeN_3C structure can reduce the energy barrier for the formation of the $^*\text{HOOCCH}_2\text{NH}_2$ intermediate, thereby accelerating the conversion of glycine oxime into glycine. This research not only provides a sustainable approach for synthesizing high-value-added organic nitrogen compounds using simple carbon and nitrogen sources but also offers a new strategy for designing new pathways for electrochemical C–N bond construction.

The structural regulation of the catalyst is the key to optimizing the reaction path. Due to the need for nitrogen reduction and carbon reduction capabilities, bimetallic catalysts can provide different catalytic sites. Liao *et al.*³⁸ have focused on a copper–bismuth bimetallic catalyst based on copper foam Cu/Bi-C@CF for the efficient electrochemical synthesis of glycine. This catalyst was derived through a metal–organic framework (MOF) array, demonstrating 89% glycine selectivity and 65.9% faradaic efficiency. The research found that the introduction of Bi changed the electronic state of Cu, reduced the binding energy of Cu, thereby altering the nitrate reduction pathway, making it more inclined to generate the key hydroxylamine intermediate rather than ammonia, and further promoting the formation of glycine. In addition, the addition of Bi also provides additional active sites for the subsequent hydrogenation reaction, enhancing the stability of

the catalyst and the synergistic effect of the multi-step tandem reaction. The research of Wu *et al.*¹⁰ proposed an electrochemical method for the reductive coupling of pyruvate and nitrate to alanine through a PdCu nanowire (PdCu NBW) electrocatalyst. This method achieves an alanine yield as high as 54.8% by integrating a series of electrochemical–electrochemical catalytic cascade processes (Fig. 3a). The research found that Cu played a key role in the process of nitrate reduction to the hydroxylamine intermediate, while Pd promoted the electrochemical reduction of pyruvate oxime to alanine. Through techniques such as *in situ* X-ray absorption spectroscopy (XAS) and *in situ* Raman spectroscopy, researchers revealed the structural evolution and changes in active sites of the catalyst during the reaction process. Furthermore, through isotope labeling experiments and comparative experiments, it was confirmed that the nitrogen in alanine originated from the electroreduction of nitrate. Li *et al.*⁴⁴ have developed an electrocatalytic system based on a PbBi dual-site alloy catalyst, revealing the pathway by which keto acids and nitrate ions form amino acids on the catalyst (Fig. 3b) and achieving efficient synthesis of various amino acids under industrial current density. By adjusting the concentration of PA (Fig. 3c), at a potential of -1.5 V vs. SCE, the FE of alanine in this catalyst reached 59.7%, the total current density reached 570 mA cm^{-2} , and it had good catalytic stability (Fig. 3d and e). Furthermore, this strategy has also been successfully applied to the synthesis of more than ten kinds of α -amino acids, showing a good prospect for industrial application. The research of Wang *et al.*³⁷ developed a method for achieving the electrochemical synthesis of glycine at industrial-grade current density using porous PbSnBi alloy catalysts. They optimized the ratio of Pb : Sn : Bi, thereby further enhancing the efficiency of the glycine electrosynthesis process (Fig. 3h). This method achieves a faradaic efficiency of up to 57.2% and a yield of $1.125\text{ mmol h}^{-1}\text{ cm}_{\text{cat}}^{-2}$ by reducing and coupling oxalic acid and nitrate in an acidic electrolyte (Fig. 3g). Research has found that by constructing multiple active sites and regulating the microenvironment on the electrode surface, the yield and selectivity of glycine can be significantly improved. Furthermore, through cyclic experiments and stability tests (Fig. 3h), it was confirmed that the catalyst has good stability in practical applications and potential industrialization prospects.

Understanding the reaction mechanism of electrocatalytic synthesis of amino acids is crucial for optimizing catalysts and improving synthesis efficiency. Li *et al.* have investigated the mechanism of electrocatalytic synthesis of glycine from nitrate and oxalic acid through density functional theory (DFT) calculations.⁴⁹ They found that the Cu–Hg enrichment site showed high activity for glycine synthesis. The formation of the C–N bond was achieved through the coupling of the amino group (NH_2^*) and GX in a local GX enrichment environment and was independent of the generation and reduction of NH_2OH (Fig. 4a–c). Furthermore, Wu *et al.*⁴² have utilized DFT calculations and *in situ* infrared spectroscopy analysis to reveal the crucial role of WO_x subnano-clusters in promoting nitrate

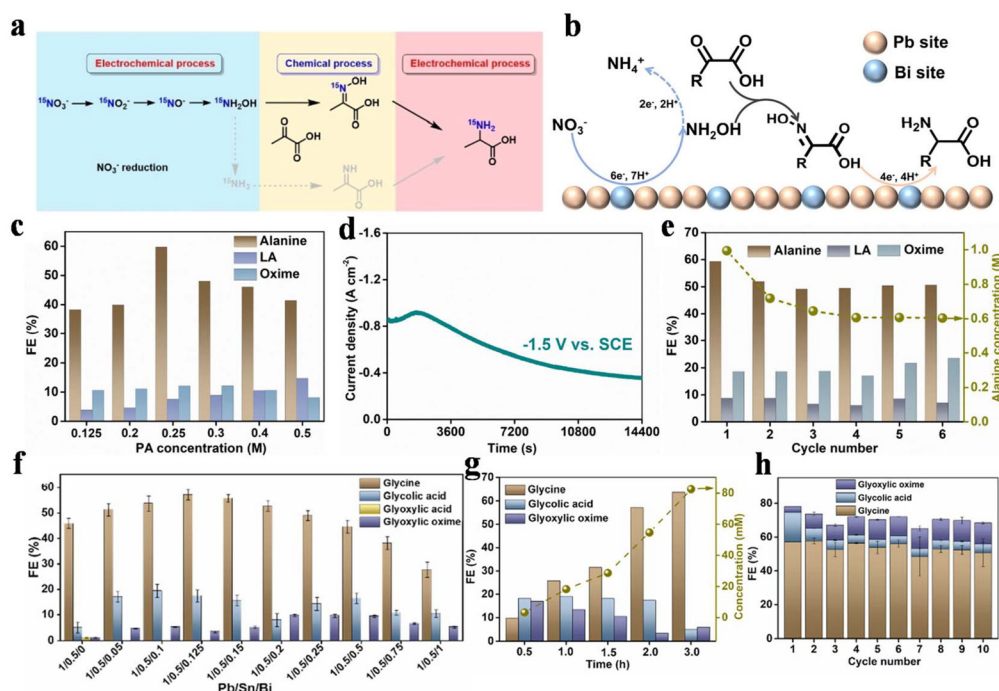


Fig. 3 (a) The reaction mechanism of C–N coupling, adapted from ref. 10 with permission from Wiley-VCH, copyright 2023. (b) Schematic illustration of the amino acid formation pathway from keto acids and nitrate on the PbBi cathode; (c) effect of PA concentration, (d) current density vs. time plot from bulk electrolysis at -1.5 V vs. SCE and (e) the recycling stability of PbBi, adapted from ref. 44 with permission from American Chemical Society, copyright 2024. (f) The effect of a porous PbSnBi cathode with different ratios on the product selectivity. (g) Variation in the glycine concentrations and faradaic efficiencies of products with the reaction time. (h) The recycling stability test for electrocatalytic co-reduction of oxalic acid and nitrate to glycine, adapted from ref. 37 with permission from Elsevier, copyright 2024.

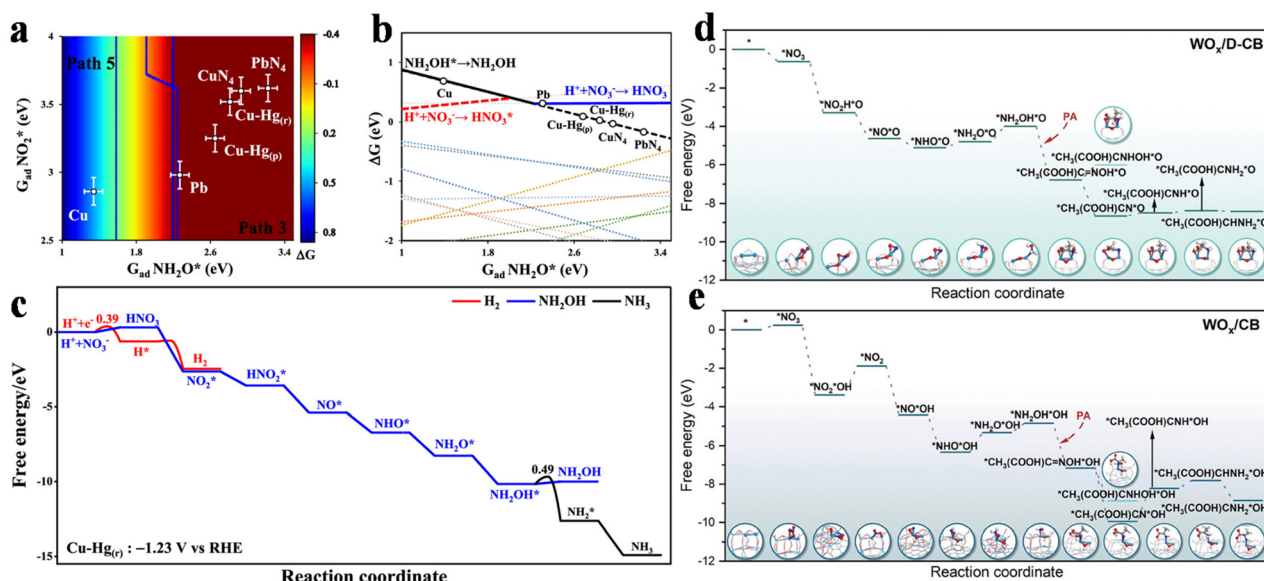


Fig. 4 (a) Two-dimensional (quasi) activity map for hydroxylamine production at -1.23 V vs. RHE , described by $G_{ad}(\text{NO}_2^*)$ and $G_{ad}(\text{NH}_2\text{O}^*)$. (b) Limiting (black and blue solid lines) and sublimiting (black and red dashed lines) steps for NH_2OH production on different catalysts. (c) Free energy diagrams of the HER, NO_3RR to NH_2OH , and NH_3 on $\text{Cu-Hg}_{(111)}$ at -1.23 V vs. RHE , adapted from ref. 49 with permission from American Chemical Society, copyright 2024. The free-energy diagram for alanine synthesis on the surface of (d) $\text{WO}_x/\text{D-CB}$ and (e) WO_x/CB . In the structural model, the red, deep blue, white, blue, and gray atomic spheres represent O, N, H, W, and C atoms, respectively; adapted from ref. 42 with permission from Wiley-VCH, copyright 2025.

reduction and their coupling with α -keto acids to form amino acids. The size of the WO_x subnanometer cluster is less than 1 nanometer, which is comparable to the Fermi wavelength of electrons, demonstrating unique electronic structures and catalytic behaviors. These sub-nano clusters form close bonds with the carbon substrate through W–O/C bonds, providing abundant active sites and thereby enhancing catalytic activity. The WO_x sub-nano clusters achieve substantial reduction of energy barriers in key steps such as NO_3^- adsorption and reduction (Fig. 4d and e), resulting in improved selectivity and efficiency of amino acid synthesis.

To enhance the efficiency of electrocatalytic synthesis of amino acids, researchers have explored various strategies. For example, Li *et al.*⁴³ have achieved the efficient synthesis of glycine from the co-reduction of oxalic acid and nitric acid by introducing an appropriate proton concentration on the surface of TiO_2 . They found that the crystal structure of TiO_2 has a significant influence on the selectivity of oxalic acid reduction to GX and nitric acid reduction to NH_2OH . By optimizing the reaction conditions, they achieved a glycine yield of 57% on the TiO_2/CNT catalyst. Furthermore, Liu *et al.*⁴⁵ have developed a Bi metal catalyst with lattice strain through electrochemical lattice engineering for the synthesis of glycine from the co-reduction of oxalic acid and nitric acid. At a potential of -0.76 V vs. RHE, the FE of glycine in this catalyst reached 79.1%, with a concentration as high as 0.17 mol L^{-1} . Experimental and theoretical calculations show that lattice strain promotes the formation of NH_2OH and the reduction of oxalate aldehyde oxime, thereby improving the synthesis efficiency of glycine. Although significant progress has been made in the electrocatalytic synthesis of amino acids in laboratory research, their application in industrial production still faces challenges. The research of Kim and his team³⁹ has proposed an electrochemical synthesis method of glycine using oxalic acid and nitrate as substrates. This method achieved a faradaic efficiency of up to 43.1% through the Cu–Hg electrode, converting carbon dioxide and nitrate waste generated by human activities into valuable glycine. Research found that under strongly acidic conditions, oxalic acid was reduced to glycolic acid, and nitrate can also generate various nitrogen-containing species. Among them, hydroxylamine and ammonia are nucleophilic and can attack the carbonyl carbon of aldehydes/ketones. Based on this, researchers explored the C–N bond formation reaction between oxalate-derived glyoxylic acid and nitrate-derived nitrogen-containing species. Efficient glycine synthesis was achieved by optimizing the reaction conditions, including controlling the electrode potential and the concentration ratio of reactants. For efficient glycine production, select a moderately negative electrode potential to avoid competition with HER while balancing reactant reduction. Furthermore, the research also revealed the significance of the concentration of reaction intermediates for the yield and selectivity of glycine. During the electrolysis process, the concentrations of oxalic acid and hydroxylamine need to reach a certain level to promote the subsequent formation of C–N bonds and the generation of glycine.

3.2.2. NO as the nitrogen source. Reaction pathway optimization and system design improve the efficiency of amino acid electrosynthesis. In the research of Li Mengyang *et al.*,¹⁴ a method for synthesizing alanine using nitric oxide (NO) and pyruvic acid (PA) on an oxide-derived silver (OD–Ag) catalyst has been proposed. This method achieved a faradaic efficiency of 17% and a yield of $11.45\text{ mmol h}^{-1}\text{ g}_{\text{cat}}^{-1}$ at normal temperature and pressure. Through a series of experiments and theoretical calculations, researchers revealed the reaction pathway of $\text{NO} \rightarrow \text{NH}_2\text{OH} \rightarrow \text{pyruvate oxime} \rightarrow \text{alanine}$ (Fig. 5a). However, due to the rapid formation and slow reduction of pyruvate oxime, various side reactions occurred, thereby reducing the yield of alanine. To address this issue, researchers designed a spatially decoupled dual-reactor system. By separating the formation and reduction reactions of pyruvate oxime, they achieved the production of 3.85 g of alanine, with a total faradaic efficiency of 70% and a purity exceeding 98%.

The design of catalysts is crucial for improving the efficiency and selectivity of electrochemical synthesis of amino acids. Xian *et al.*⁴⁷ have prepared a method for converting NO into various α -amino acids using a self-supporting carbon fiber membrane modified by the CoFe alloy CoFe–SSM. This method not only achieved a faradaic efficiency of 32.4% and a leucine yield of $115.4\text{ }\mu\text{mol h}^{-1}$ but also demonstrated an ultra-long stability of more than 240 hours (Fig. 5b and c). The researchers revealed the reduction process of NO on CoFe–SSM through *in situ* X-ray absorption fine structure (XAFS) and synchrotron radiation infrared spectroscopy (SRIR) analyses. The key steps among them are the formation of NH_2OH and the coupling reaction with α -keto acid (Fig. 5d and e). The same team has investigated another catalyst, applying a nitrogen-doped carbon-supported atomically dispersed iron catalyst (AD–Fe/NC) derived from the metal–organic framework (MOF) to achieve highly selective synthesis of essential amino acids.⁴⁸ The catalyst with the active site of Fe– N_4 was obtained through Fe doping of Zn-based MOF (MET-6) and high-temperature carbonization. Under the condition of -0.6 V vs. RHE, AD–Fe/NC catalyzed the reaction of 3-methyl-2-oxybutyric acid with NO to generate valine, with a yield of $32.1\text{ }\mu\text{mol mg}_{\text{cat}}^{-1}$ and a selectivity of 11.3% (Fig. 5f and g). *In situ* characterization revealed that the reaction pathway was as follows: NO was adsorbed at the Fe site and reduced to NH_2OH , then condensed with α -keto acid to form oxime, and finally hydrogenated into amino acids (Fig. 5h and i). This catalyst is applicable to multiple nitrogen sources and can synthesize six essential amino acids (such as leucine and alanine). Although there is still room for improvement in the current yield, its atomically dispersed active sites provide a new perspective for understanding the C–N coupling mechanism.

The mechanism studies of these several studies indicate that the common pathway for efficient amino acid synthesis is $\text{NO} \rightarrow \text{NH}_2\text{OH} \rightarrow \text{oxime intermediate} \rightarrow \text{hydrogenation product}$. The performance differences of catalysts result from three factors: (1) the stability ability of active sites for key inter-

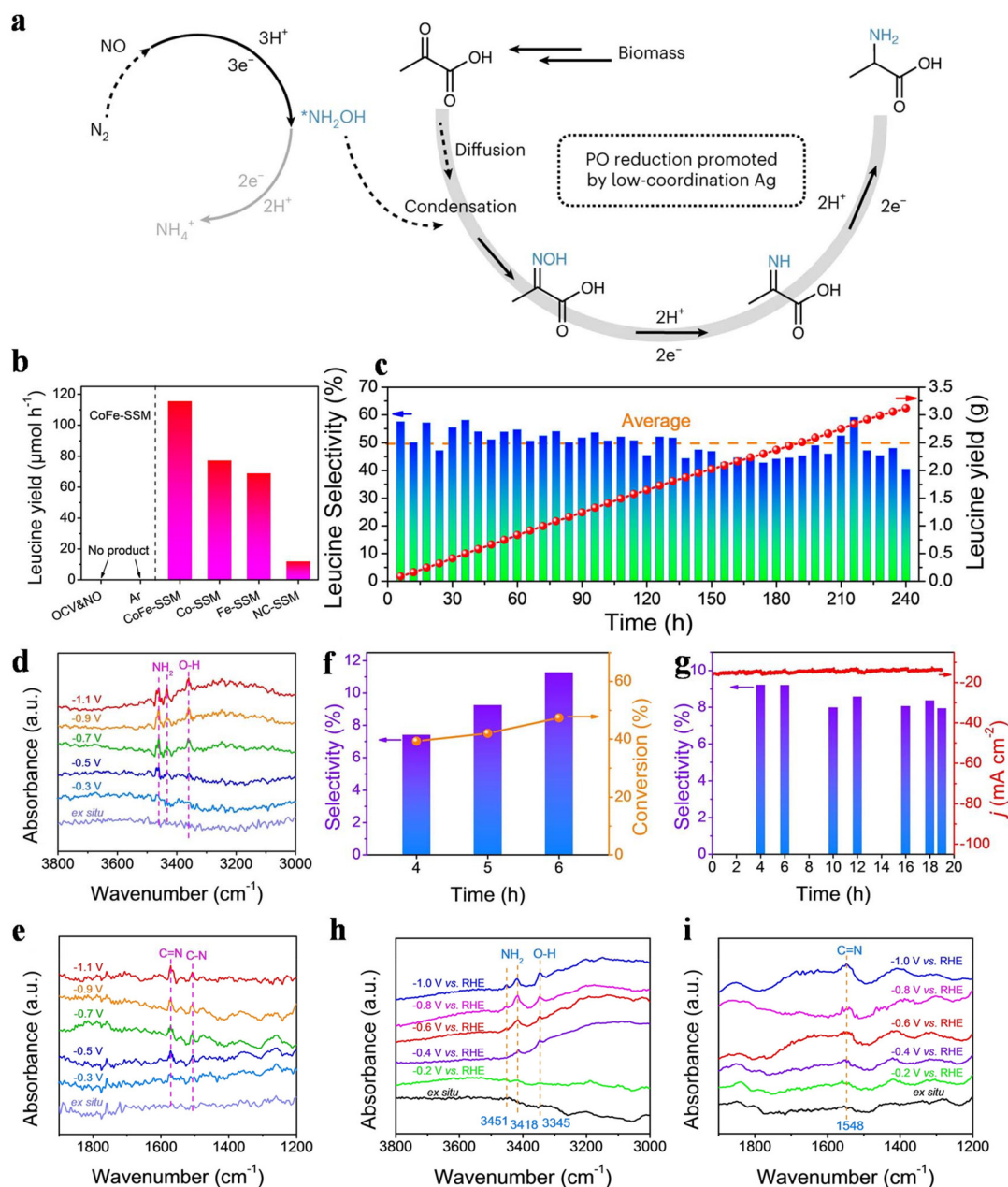


Fig. 5 (a) Schematic illustration of the alanine generation pathway on the OD-Ag surface, adapted from ref. 14 with permission from Springer Nature, copyright 2023. (b) The yield of leucine under different test conditions with CoFe-SSM and control specimens; (c) the long-term stability test for leucine production on CoFe-SSM; (d) 3000–3800 cm^{-1} and (e) 1200–1900 cm^{-1} versus potentials for CoFe-SSM under working conditions, adapted from ref. 47 with permission from Wiley-VCH, copyright 2023. (f) Electrochemical valine synthesis performance of AD-Fe/NC and bare GC under different conditions. (g) The long-term stability test for electrocatalytic co-reduction of 3-methyl-2-oxobutanoic acid and NO to valine. (h) 3000–3800 cm^{-1} and (i) 1200–1900 cm^{-1} versus potentials for AD-Fe/NC under working conditions, adapted from ref. 48 with permission from Wiley-VCH, copyright 2023.

mediates (such as NH_2OH); (2) the regulatory role of the microstructure on the mass transfer process; and (3) the degree of reduction of the C–N coupling energy barrier by the electronic structure. Future research requires sustained breakthroughs in aspects such as the design of atomic-level active sites, the regulation of the microenvironment at reaction interfaces, and the optimization of reaction pathways.

3.2.3. NH_3 as the nitrogen source. Xiao's team has developed ball-milled carbon nanotube (BM-CNTs) catalysts,²⁰ constructing abundant inherent defects in the carbon framework through mechanochemical strategies. This material exhibits outstanding performance in the α -keto acid reduction amination reaction (Fig. 6a). Taking the synthesis of glutamic acid from 2-ketoglutaric acid as the model reaction, it achieved a

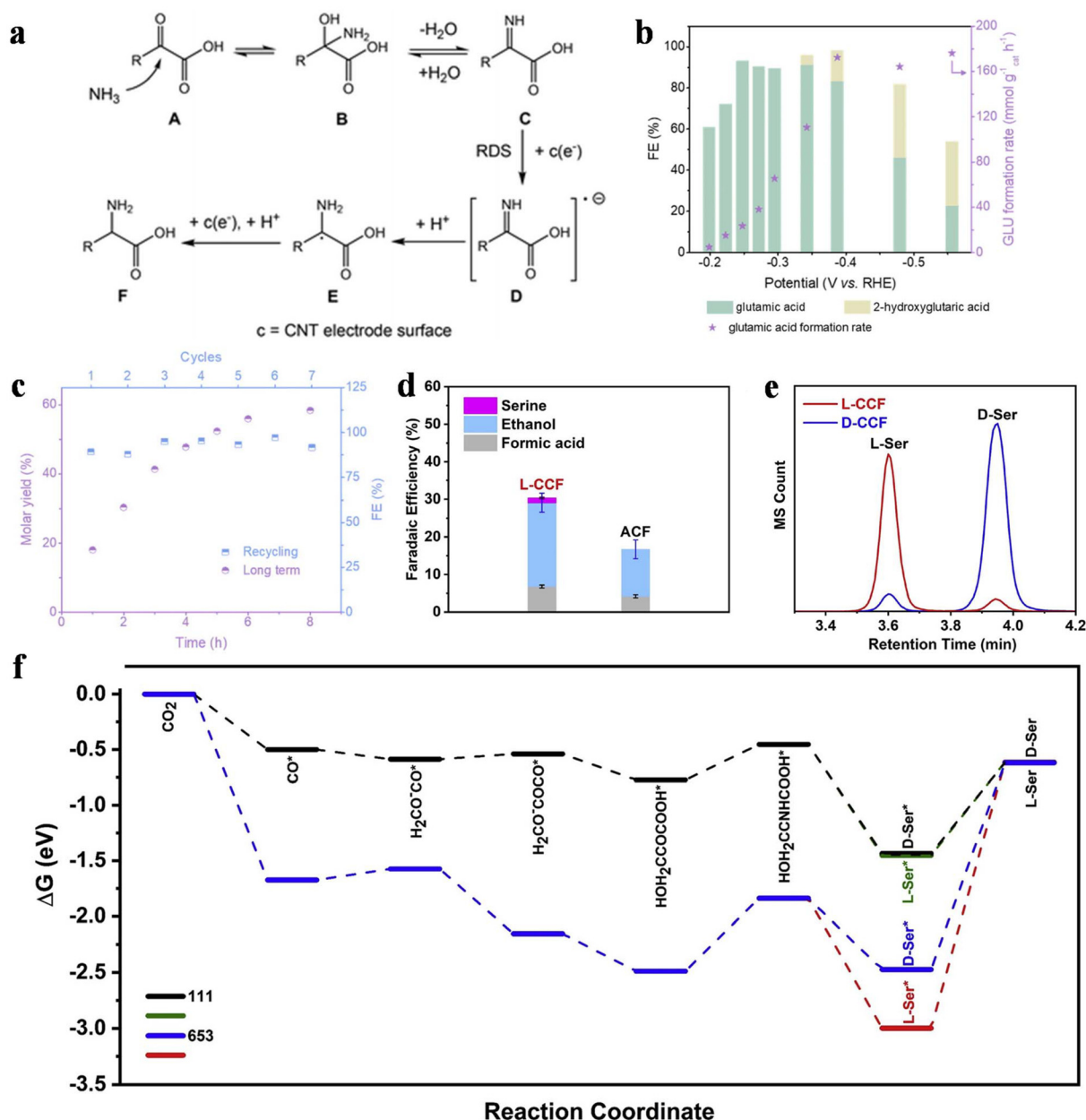


Fig. 6 (a) The glutamic acid synthesis mechanism on BM-CNTs. (b) The FE and GLU formation rate in the BM-CNTs catalyzed room-temperature constant potential electrolysis of 2-ketoglutaric acid for 1 h at different applied potentials. (c) Extended duration room-temperature electrolysis (violet dots) and recycling test (blue dots) over BM-CNTs, adapted from ref. 20 with permission from the Royal Society of Chemistry, copyright 2023. (d) FEs of Ser, ethanol, and formic acid in the L-CCF and ACF catalytic systems. (e) HPLC-MS of Ser obtained with L- and D-CCFs in 0.25 M NH_4HCO_3 under 4.5 MPa CO_2 at a CV potential between 0.6 and 1.3 V versus the reversible hydrogen electrode (RHE) for 24 h. (f) The Gibbs free energy profiles for the intermediates of CO_2 reduction on Cu(653)⁵ and Cu(111), adapted from ref. 22 with permission from Elsevier, copyright 2022.

faradaic efficiency of approximately 90% and a reaction rate of $180.9 \text{ mmol g}^{-1} \text{h}^{-1}$ at -0.39 V vs. RHE , and the molar yield of electrolysis after 8 hours reaches 60% (Fig. 6b and c). Extended experiments show that BM-CNTs are also effective for the synthesis of long-carbon-chain amino acids. The mechanism by which their hydrophobic surface characteristics enhance substrate adsorption opens up a direction for the

design of new catalysts. Kinetic analysis reveals that, unlike metal catalytic pathways, the reaction rate of this system is controlled by the first electron transfer step of the imine intermediate. This discovery provides a new perspective for the mechanism study of carbon-based catalysts.

Through the design of chiral copper thin film (CCFs) electrodes, the team of Fang has achieved a breakthrough in direct

electrocatalytic synthesis of amino acids from CO_2 and NH_3 .²² The research team used histidine-induced electrodeposition to prepare copper thin films with chiral knot sites, achieving a substantial reduction in the reaction energy barrier of C_{3+} products. Experiments showed that serine (Ser) was the main product, with an optical purity (ee value) of over 90% and a faradaic efficiency of 1.2% (Fig. 6d and e). Theoretical calculations revealed that the chiral site stabilized the intermediate 3-hydroxypropionic acid, promoting the formation of L-serine (Fig. 6f). This work was the first to achieve electrocatalytic CO_2 reduction for the synthesis of chiral biomolecules, providing a new strategy for the artificial synthesis of complex biomolecules.

4. Outlook

At present, research on the electrosynthesis of amino acids is still in its early stages. To narrow this gap with practical applications, we seek directions for future improvement, including the utilization of sustainable raw materials, innovative catalyst design, a deeper understanding of reaction pathways, and optimized reactor configurations.

4.1. Substrate source

The sustainable sourcing of raw materials is crucial for the economic and environmental viability of electrocatalytic amino acid synthesis. Utilizing waste streams such as industrial exhaust gases, wastewater, and discarded plastics can transform these by-products into valuable resources. For example, nitrate and nitric oxide can be sourced from industrial wastewater and exhaust gases, while oxalic acid can be produced from the electrocatalytic oxidation of ethylene glycol, a by-product of PET plastic hydrolysis. Direct carbon dioxide capture from air offers a sustainable carbon source for synthesis. These approaches not only reduce waste but also align with the goals of the circular economy and carbon neutrality. The future of electrocatalytic amino acid synthesis lies in the strategic utilization of sustainable raw materials. By leveraging industrial waste, capturing CO_2 from the air, and upcycling waste plastics, the industry can achieve significant environmental benefits while maintaining economic viability. These approaches not only reduce waste but also contribute to a more sustainable and circular chemical manufacturing industry.

Utilizing nitrogen from the air as a nitrogen source for the electrocatalytic synthesis of amino acids is an ideal approach for achieving a fully green and sustainable synthesis process. In recent years, two cascade pathways based on renewable electricity have shown great potential. The first pathway draws inspiration from the Haber-Bosch process: nitrogen is first reduced to ammonia *via* a lithium-mediated electrochemical process, followed by selective oxidation of ammonia to hydroxylamine using electrosynthesis generated hydrogen peroxide, and finally, hydroxylamine reacts with aldehyde acids such as glyoxylic acid derived from carbon dioxide through

spontaneous oximation and subsequent electroreduction to produce amino acids, for instance, glycine.²⁸ The advantage of this route lies in the separation of steps, which facilitates purification of intermediates, thus achieving nitrogen atom selectivity as high as 98.7%. However, its bottleneck is the low faradaic efficiency of nitrogen electroreduction to ammonia, only 18%, coupled with the complexity of the multi-step reaction sequence, which increases system energy consumption and cost. The second pathway takes a different approach, adopting a “first oxidation, then reduction” strategy: nitrogen in air and water is directly converted into nitric acid by plasma discharge technology, and then under mild conditions, the nitric acid is reduced to hydroxylamine with high selectivity using a bismuth-based catalyst, with a faradaic efficiency of up to 81.0%. This pathway uses extremely simple raw materials—air and water—under mild reaction conditions, avoiding precious metal catalysts and high-temperature, high-pressure processes and demonstrating excellent atom economy and sustainability.⁵⁰ However, challenges for practical applications include the energy efficiency of the plasma step, the stability of the equipment, and the possible downstream separation energy demands caused by the relatively low concentration of the resulting nitric acid solution. In summary, these two pathways outline a clear blueprint for “from air to amino acids” green synthesis. Future research should focus on either developing efficient nitrogen electroreduction catalysts to optimize the first pathway or improving plasma efficiency and reactor design to overcome the bottlenecks of the second pathway, ultimately achieving economically viable amino acid electrosynthesis.

4.2. Catalyst design

Future advancements in electrocatalytic amino acid synthesis will rely on the rational design of catalysts to address current limitations in selectivity, stability, and multi-step reaction synergy. The development of catalysts capable of efficiently mediating C–N bond formation while suppressing the side reaction remains a key driving force of this field. Atomically dispersed or single-atom catalysts have emerged as promising candidates due to their maximized atomic utilization and tunable electronic structures. It should be noted that single-atom catalysts face challenges such as metal aggregation at high current densities and the easy detachment of active sites in strong acid environments. To solve these problems, we can optimize the coordination environment (for example, by introducing S or P dopants) to enhance metal anchoring and construct core-shell structures to isolate the corrosive environment. C–N coupling electrosynthesis of amino acids involves a series of complex reactions, and bimetallic or trimetallic catalysts with spatially isolated active sites provide a strategic approach for decoupling nitrogen reduction, carbon hydrogenation, and C–N bond formation, which can enhance product selectivity. Future research requires exploration of ternary systems^{51–53} to resolve kinetic mismatch in multi-electron processes. In this process, optimizing the synergistic effect is crucial, particularly with regard to the charge transfer behavior

between metal atoms. Rational regulation of these effects enables stabilization of hydroxylamine intermediates, prevents excessive reduction to ammonia, and improves product selectivity.

In bimetallic or trimetallic catalysts, the design strategy of “spatially isolating the nitrogen reduction site from the oxime hydrogenation site” is crucial for optimizing the tandem reaction pathway and enhancing the selectivity of amino acid synthesis. The core of this strategy lies in spatially decoupling the two key steps, nitrogen source reduction and hydrogenation of the carbon–nitrogen intermediate, enabling the matching of the most suitable active center for each reaction. This addresses their inherent kinetic mismatch and suppresses side reactions. Specifically, the ideal catalyst design involves one metal site (*e.g.*, Cu, Bi, or Fe) preferentially adsorbing and activating the nitrogen source (such as NO_3^- or NO), efficiently reducing it to hydroxylamine (NH_2OH) or directly coupling it with the carbon source, while simultaneously inhibiting its over-reduction to NH_3 . Another spatially adjacent yet electronically distinct metal site (*e.g.*, Pd, Ag, or Cu) is dedicated to adsorbing the oxime intermediate, formed from the condensation of hydroxylamine and α -keto acid, and promoting its efficient hydrogenation into the target amino acid. Such site isolation effectively prevents key intermediates from experiencing competitive adsorption or non-selective decomposition on a single active site. Future advancement of this strategy requires combining advanced characterization techniques with theoretical calculations to precisely elucidate the synergistic mechanisms and distance effects between the dual sites. Further exploration into achieving more complex spatial isolation within ternary alloys or core–shell structures is also needed to achieve precise control over multi-step tandem reactions, including carbon source reduction.

In addition to the existing research directions on catalysts, the development of chiral catalysts also shows great potential and can be considered one of the key research directions. Recently, a breakthrough was achieved with histidine-functionalized copper films, which exhibited a more than 90% enantiomeric excess (ee) value in the synthesis of serine.²² This achievement brings hope for the enantioselective synthesis of non-classical amino acids and is expected to meet the demand for optical purity in the pharmaceutical field.

The design of efficient and selective catalysts is a cornerstone of electrocatalytic synthesis. Classical trial-and-error approaches are time-consuming and resource-intensive. Machine learning and artificial intelligence can accelerate the discovery of new catalysts by predicting the performance of various materials based on their electronic and structural properties.⁵⁴

4.3. Mechanism investigation

The optimization of the reaction pathway is crucial for overcoming the inherent kinetic mismatch and the instability of intermediates in multi-step amino acid synthesis.

Through theoretical methods such as density functional theory (DFT) calculations, the key steps and influencing

factors in the reaction process can be revealed. For instance, in the electrosynthesis of glycine, research has found that its mechanism involves the reduction of nitrate to hydroxylamine and oxalic acid to glyoxylic acid, as well as the coupling reaction of hydroxylamine and glyoxylic acid.⁴⁹ These studies provide theoretical guidance for the design of catalysts and help us find more efficient catalysts. The selection and design of catalysts play a decisive role in the efficiency and selectivity of amino acid electrosynthesis. Studies show that different catalysts have a significant impact on the activity and selectivity of the reaction. For example, the Cu–Hg(r) surface⁴⁹ exhibits good activity and selectivity in the electrosynthesis of glycine, which is attributed to its good balance of thermochemical and electrochemical steps. In addition, Ag has been found to be an ideal catalyst for glycine electrosynthesis.⁵⁵ Its unique weak adsorption properties enable it to activate the reaction intermediate glyoxylic acid oxime, thereby achieving an efficient hydrogenation reaction.

In the future, we can systematically trace the complete reaction pathway from NO_3^- to amino acids *via* NH_2OH and oxime intermediates using DFT calculations, analyse the free energy changes at each step, identify the rate-determining step, and elucidate the key role of the catalyst's electronic structure (such as the d-band center and charge distribution) in suppressing competing side reactions. Based on this mechanistic understanding, key physical descriptors (*e.g.*, adsorption energies of intermediates and differences in reaction energy barriers) can be extracted and used as input features, along with catalyst elemental composition, structural characteristics, and reaction conditions, to construct machine learning models. We will develop multi-output regression models with faradaic efficiency and product selectivity of the target amino acids as the core optimization objectives. Ultimately, by integrating active learning and Bayesian optimization strategies, efficient and precise screening of catalyst compositions and performance prediction can be achieved, advancing the design and development of high-performance electrocatalysts for amino acid synthesis.

The electrocatalytic synthesis of amino acids can also form a cascade system with other catalytic methods, such as thermocatalysis and enzymatic reactions, integrating various advantages to enhance synthesis efficiency. In the cascade system, thermocatalysis can achieve the oxidative depolymerization of PET, rapidly generating high-purity OA, which provides key raw materials for subsequent electrocatalytic synthesis of amino acids.³² By using thermocatalysis and electrocatalysis in tandem, an efficient, green, and economical conversion from PET to glycine can be achieved, realizing waste upgrading, precise synthesis, and high-value conversion. Although electrocatalytic technology can achieve selective control over specific reactions by adjusting the potential, its selectivity level still needs improvement. In contrast, biological enzymes exhibit high catalytic efficiency in the conversion of complex biomolecules due to their excellent substrate specificity and stereoselectivity; meanwhile, electrocatalysis shows greater advantages when dealing with simple substrates. Existing

research has confirmed that carbon dioxide can be converted into acetic acid and ethanol through electrocatalysis, which can then be further converted into tyrosine by genetically engineered *Escherichia coli*.⁵⁶ This enzyme-electro synergy catalytic strategy not only expands the range of applicable reaction substrates but also realizes the conversion pathway from low-cost raw materials (such as carbon dioxide and biomass) to high-value products, providing new ideas for enhancing process economics.

4.4. System optimization

The choice of reactor configuration significantly impacts the efficiency and scalability of the synthesis process. Membrane electrode assemblies (MEAs) and flow cells offer advantages such as high current densities, improved mass transfer, and better control over reaction conditions, making them more suitable for industrial applications.²⁸ Reactors separated in space or time mitigate cross-interference between intermediates. For example, dual-reactor configurations isolate NH_2OH generation (*via* NO reduction) from subsequent C–N coupling steps, achieving FE > 70% for glycine synthesis.¹⁴ Through rational design of the reaction system, the reaction efficiency and product purity can undergo substantial improvement. Future research can explore more similar decoupling designs to address efficiency and selectivity issues in other complex reactions.

Apart from reactor design, pulse electrolysis^{57,58} and electrolyte pH regulation^{59,60} are two key optimization strategies that can synergistically enhance synthesis efficiency by improving reaction pathways and the interfacial microenvironment. In multi-step electrochemical synthesis, reactants must pass through multiple intermediate states, and the reaction pathway is often constrained by factors such as intermediate coverage and local pH changes. Pulsed electrolysis alternates between cathodic and anodic potentials, enabling dynamic regulation of intermediate coverage on the catalyst surface, thereby promoting key steps such as C–N coupling.⁶¹ In direct current electrolysis, the electrode surface often experiences local pH deviations due to proton consumption or generation (*e.g.*, surface pH rise caused by the hydrogen evolution reaction), which can affect reaction stability and selectivity. The off-period in pulsed electrolysis provides a time window for the diffusion of protons and hydroxide ions, allowing the surface pH to re-homogenize, which helps stabilize pH-sensitive intermediates. On the other hand, the electrolyte pH has a decisive impact on the interfacial water structure, proton transfer pathways, and intermediate stability. Taking the electrochemical reduction of nitrate to synthesize hydroxylamine (NH_2OH) as an example, NH_2OH tends to undergo deep hydrogenation to form NH_3 in near-neutral or alkaline environments, leading to a decrease in the selectivity of the desired product.⁶² Pulsed electrolysis, through its unique spatiotemporal regulation capability, mitigates local pH fluctuations and optimizes the co-adsorption of intermediates, while a reasonable setting of the system pH ensures the stability of key intermediates from both thermodynamic and mass transfer perspectives.

Combining the advantages of both approaches can provide an effective pathway for the integrated optimization of amino acid electrosynthesis systems, offering both dynamic adaptability and steady-state controllability.

In summary, the future of electrocatalytic amino acid synthesis lies in the integration of sustainable raw materials, advanced catalyst design, detailed reaction pathway studies, and optimized reactor configurations. These advancements will not only improve the efficiency and selectivity of the process but also contribute to a more sustainable and circular chemical manufacturing industry.

Author contributions

Xulin Nong: investigation, visualization, writing – original draft, writing – review and editing, and formal analysis. Chunqi Yang: investigation, visualization, writing – review and editing, and formal analysis. Jingwen Zhuang: writing – review and editing and formal analysis. Yuhang Li: investigation, visualization, writing – review and editing, formal analysis, supervision, funding acquisition, conceptualization, and the lead of contribution. Chunzhong Li: investigation, visualization, writing – review and editing, formal analysis, supervision, funding acquisition, conceptualization, and the lead of contribution.

Conflicts of interest

The authors declare that they have no conflicts of interest in this work.

Data availability

The data supporting the findings of this study are available from the corresponding author upon reasonable request.

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