Proceedings of the 4th International Conference on Functional Materials and Civil Engineering
DOI: 10.54254/2755-2721/2026.35070

Mechanistic Insights into Electrocatalytic NO_x-to-Glycine Conversion

Yuchen Tian

School of Materials Science and Engineering, Hebei University of Technology, Tianjin, China
13131280557@163.com

Abstract. Amino acids are high-value chemicals widely used in the food, pharmaceutical, and agricultural industries, but their conventional synthesis routes often carry a substantial carbon footprint. Electrocatalytic conversion of nitrogen oxides (NO_x) into amino acids represents a promising sustainable alternative. Among the possible products, glycine is an important model system for understanding the fundamentals of NO_x-derived amino acid electrosynthesis. However, achieving high selectivity remains difficult because NO_x reduction involves multiple reactive intermediates and competing reaction pathways, leading to complex product distributions. These challenges make mechanistic understanding and advanced characterization central to progress in the field. This review examines glycine electrosynthesis as a representative case to uncover key mechanistic aspects of electrocatalytic NO_x reduction. It discusses how characterization techniques, including vibrational spectroscopy, mass spectrometry, electron paramagnetic resonance, and X-ray-based methods, enable the detection of intermediates and the elucidation of reaction pathways. The paper also analyzes how catalyst structure and reaction conditions, especially pH, regulate intermediate evolution, C–N coupling, and glycine formation. Finally, current challenges and future opportunities are summarized, aiming to provide guidance for the rational design of selective electrocatalysts for NO_x-to-amino acid conversion.

Keywords: Electrocatalytic NO_x Reduction, C–N Coupling, Glycine Electrosynthesis, Hydroxylamine Intermediate, In Situ Characterization

1. Introduction

Amino acids are fundamental building blocks of proteins and serve as indispensable nutrients, pharmaceuticals, and chemical feedstocks in the food, agriculture, and biomedical sectors [1]. As global demand for amino acids continues to grow, concerns have intensified over the sustainability of their production [2]. At present, amino acid manufacture relies mainly on Strecker synthesis and microbial fermentation. However, these conventional routes are often constrained by high energy consumption, substantial carbon emissions, complex downstream purification, and dependence on fossil-derived or biologically fixed nitrogen sources [1]. Developing a sustainable and economically viable strategies for amino acid synthesis therefore remains an important challenge.

Nitrogen oxides (NO_x), emitted in large quantities from combustion processes and industrial activities, are typically regarded as harmful pollutants [3]. Yet these species also represent abundant and low-cost nitrogen feedstocks. Converting NO_x from an environmental liability into a chemical resource offers a particularly attractive opportunity, as it could couple pollutant mitigation with the production of value-added nitrogen-containing chemicals [4]. Among the possible products, ammonia (NH_3) and amino acids are especially appealing because of their high industrial value and central importance to the emerging nitrogen economy.

Electrocatalytic NO_x reduction has recently emerged as a promising route for achieving such transformations under mild conditions using renewable electricity [3]. In contrast to conventional thermocatalytic denitrification, which generally requires high operating temperatures, large energy input, and may generate secondary pollution, electrocatalytic approaches offer greater flexibility in controlling product formation [3]. Reaction selectivity can, in principle, be tuned through the applied potential, electrolyte environment, catalyst composition, and surface structure. These features make electrocatalysis particularly attractive for steering NO_x conversion toward specific nitrogen-containing products, including NH_3, hydroxylamine (NH_2OH), and amino acids such as glycine.

Despite this promise, achieving selective NO_x-to-amino acid conversion remains highly challenging [3]. The electroreduction of NO_x involves numerous nitrogen-containing intermediates, many of which are highly reactive and can undergo parallel or sequential transformations under similar reaction conditions [1]. The coexistence of multiple intermediates and competing pathways makes it difficult to control product distribution and, in particular, to direct the reaction toward a single amino acid product. This mechanistic complexity is a central obstacle in the field and highlights the need for a deeper understanding of intermediate generation, interconversion, and C–N bond formation [5]. In this context, mechanistic analysis and advanced operando or in situ characterization become indispensable for identifying active intermediates, elucidating pathway competition, and uncovering the factors that govern selectivity [3].

In this review, glycine electrosynthesis is taken as a representative case to examine the mechanistic foundations of electrocatalytic NO_x conversion to amino acids. By focusing on the evolution of active sites, the identification of key intermediates, and the elementary steps involved in C–N coupling, the paper aims to clarify the relationships among catalyst structure, reaction pathway, and product selectivity. Particular attention is given to how catalyst design and reaction conditions regulate intermediate speciation and direct the formation of glycine. Through this perspective, the review seeks to provide mechanistic insight and methodological guidance for the rational design of selective electrocatalysts for NO_x-to-amino acid conversion.

2. Fundamentals of electrocatalytic NO_x reduction and catalyst design for selective glycine electrosynthesis

Electrocatalytic reduction of NO_x proceeds via a proton-coupled electron transfer process, in which nitrogen-containing substances in a high oxidation state are stepwise reduced through the sequential uptake of electrons and protons at the catalyst surface [6]. The selectivity of the overall reaction is governed by the synergistic interaction between applied potential, electrolyte pH and catalyst surface structure, all of which influence the speciation, surface adsorption, and subsequent transformation of key intermediates. Among the various intermediates formed during NO_x electroreduction, nitrite (NO_2^-) and NH_2OH are particularly important. Differences in their intrinsic relative stability, surface binding strength, and reactivity can strongly affect pathway evolution, leading to distinct reduction routes and, ultimately, significant differences in product selectivity.

In the context of glycine electrosynthesis, the reaction proceeds through a well-defined three-step pathway, as shown in Figure 1. First, NO_x is electrochemically reduced on the catalyst surface to produce NH_2OH (conversion of 3 to 4, Figure 1). Second, NH_2OH undergoes spontaneous C–N coupling with a carbon source, typically glyoxylate (molecule 2 in Figure 1) or oxalic acid (molecule 1 in Figure 1), to form an oxime intermediate (2 + 4 → 5, Figure 1). Finally, the oxime is further hydrogenated to yield the target amino acid (conversion of 5 to 6, Figure 1) [7]. Within this sequence, the selective and sustained generation of NH_2OH is the key bottleneck, because both its over-reduction to NH_3 and its insufficient formation can significantly suppress glycine yield. Accordingly, catalyst design is central to stabilizing the NH_2OH intermediate while promoting subsequent C–N coupling and hydrogenation steps. Different catalyst systems therefore exhibit marked differences in Faradaic efficiency and reaction rate, depending on the nature of nitrogen source, carbon source, and electrolyte conditions.

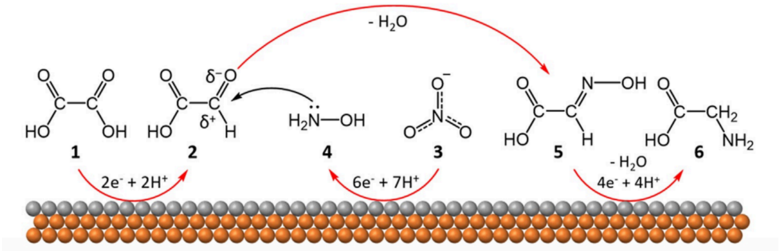

Figure 1. Glyoxylic oxime-involved pathway of glycine production from oxalic acid and nitrate on the Cu-Hg cathode. [The red and black arrows indicate the direction of the reactions and flow of electron pairs, respectively (1: oxalic acid, 2: glyoxylic acid, 3: nitrate, 4: hydroxylamine, 5: glyoxylic oxime, 6: glycine). Adapted from Ref. [8], copyright 2021, with permission from Wiley-VCH.]

Table 1. Summary of the performance of catalysts toward glycine products

Catalyst	Electrolyte	Nitrogen source	Carbon source	Reaction rate	Potential	Faradaic efficiency	Reference
N-C SSM	0.1 M HCl	NO	glyoxylic acid	$11.9\ \mu mol\cdot h^{-1}$	-0.7 V	—	[3]
CoFe-SSM	0.1 M HCl	NO_x	glyoxylic acid	$115.4\ \mu mol\cdot h^{-1}$	-0.7 V	27.3%	[3]
AD-Fe/N	0.1 M HCl	NO	glyoxylic acid	Yield 14.8 $\mu mol\cdot mg^{-1}$	-0.6 V	—	[4]
Fe–N–C-700	0.5 M oxalic acid	NO_3^-	oxalic acid	—	-1.0 V	—	[1]
Co-HCNF	0.1 M HCl	NO_3^-	glyoxylic acid	$222.3\ \mu mol\cdot h^{-1}$	-0.7 V	41.7% 42.8%	[9]
CuSn/C	0.5 M Na_2SO_4 aqueous solution	NO_3^-	glyoxylic acid	Yield 39.83 $\mu mol\cdot cm^{-2}\cdot h^{-1}$	-0.2 V	78.69%	[10]
TiO2	0.5 M H_2SO_4	NH_2OH	oxalic acid	—	-0.7 V	20%	[8]
calcination of Ti foil	0.1 M HCl	$(NH_2OH)_2\cdot H_2SO_4$	glyoxylic acid	—	-0.7 V	56% C	[8]

Table 1. (continued)

d-Bi	0.1 M H_2SO_4	NO_3^-	oxalic acid	Yield 3.6 $mol \cdot h^{-1} \cdot g^{-1}$	-1.3 V	81.1%	[2]
IL@Bi	0.3 M H_2SO_4	NO_3^-	oxalic acid	—	—	78.9%	[5]

Note: SSM: self-standing membrane; HCNF: hollow carbon nanofiber; AD-Fe/N: Atomically dispersed Fe/N-doped carbon; IL@Bi: ionic liquid-modified bismuth catalyst; C: carbon selectivity; —: not reported.

The choice of carbon source fundamentally determines the reaction pathway and catalyst requirements in glycine electrosynthesis. To date, two main strategies have been explored: the direct use of glyoxylic acid as the carbon source, and indirect routes in which oxalic acid is first electrochemically reduced in situ to glyoxylic acid (Table 1). Although both strategies ultimately converge at the same key C–N coupling step between glyoxylic acid and NH_2OH, they differ substantially in the number of electrochemical transformations involved and in the associated catalytic challenges.

When glyoxylic acid is supplied directly, its condensation with NH_2OH can proceed spontaneously without additional electrochemical activation. Under these conditions, the primary challenge lies in the selective and sustained generation of NH_2OH. Because NH_2OH is highly reactive and readily undergoes further reduction to NH_3, suppressing this over-reduction is essential for achieving high glycine selectivity. Accordingly, catalyst design must focus on stabilizing NH_2OH at the catalyst surface while maintaining sufficient activity for its efficient coupling with glyoxylic acid. As illustrated in Figure 1, this process follows a stepwise route where nitrate reduction to NH_2OH precedes spontaneous condensation with glyoxylic acid, followed by electrohydrogenation to glycine. Several catalyst systems have demonstrated this principle. For example, CoFe-SSM takes advantage of bimetallic synergy to stabilize NH_2OH and inhibit its excessive reduction, thereby favoring glycine formation [3]. Similarly, AD-Fe/N, featuring atomically dispersed Fe-N_4 sites, enables precise regulation of the nitrate reduction pathway by controlling the extent of electron transfer, stabilizing the NH_2OH intermediate, and promoting rapid C–N coupling with glyoxylic acid [4]. As a result, product selectivity is significantly improved. The stabilization mechanism of this intermediate has been directly elucidated through in situ X-ray absorption fine structure (XAFS) and synchrotron-based infrared spectroscopy [4]. In a related manner, Co-HCNF also achieves pathway selectivity through a well-defined metal coordination environment, further highlighting the importance of local electronic and structural regulation in controlling NH_2OH generation and subsequent glycine synthesis [9].

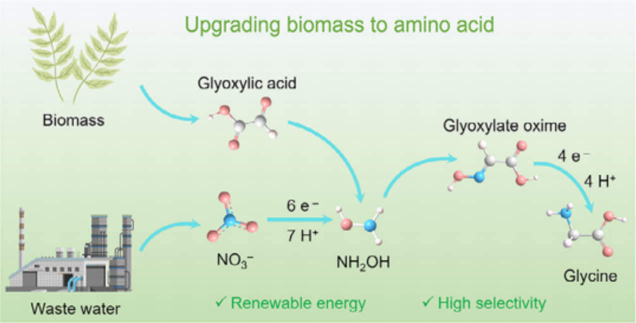

Figure 2. Schematic illustration of the reaction mechanism for electrocatalytic coupling of biomass conversion and nitrate reduction to glycine. [Adapted from Ref. [10], copyright 2025, with permission from Wiley-VCH.]

When oxalic acid is used as the carbon source, glycine electrosynthesis involves an additional electrochemical step: the reduction of oxalic acid to glyoxylic acid. This process must be kinetically coupled with NO_x reduction and subsequent C–N coupling within the same system, thereby introducing greater mechanistic complexity. As illustrated in Figure 2, the overall pathway includes CO_2/oxalic acid reduction to glyoxylic acid, nitrate reduction to NH_2OH, their spontaneous condensation to form glyoxylic acid oxime, and final electroreduction to glycine, alongside competing deep-reduction side reactions. Even so, several catalyst strategies have shown clear effectiveness. Fe–N–C single-atom catalysts achieve tandem selectivity through intermediate trapping; IL@Bi employs imidazolium-derived radicals as selective mediators to direct C–N coupling toward glycine [5]; d-Bi uses its high-surface-area morphology to strengthen intermediate adsorption [2]; and CuSn/C leverages Cu-Sn electronic interactions to stabilize NH_2OH against over-reduction. Although these systems differ in mechanistic detail, they converge on the same central challenge: preventing the premature loss of NH_2OH before C–N coupling occurs [10]. As illustrated in Figure 3, the IL@Bi catalyst addresses this challenge through a relayed electron transfer mechanism. Electrons are initially transferred from Bi to $Emmim^+$, forming the Emmim· radical, which then donates electrons to glyoxylic oxime (GAO) via hydrogen-bonding interactions, enabling fast conversion to glycine. This relayed pathway shows faster kinetics compared to direct electron transfer from Bi to GAO.

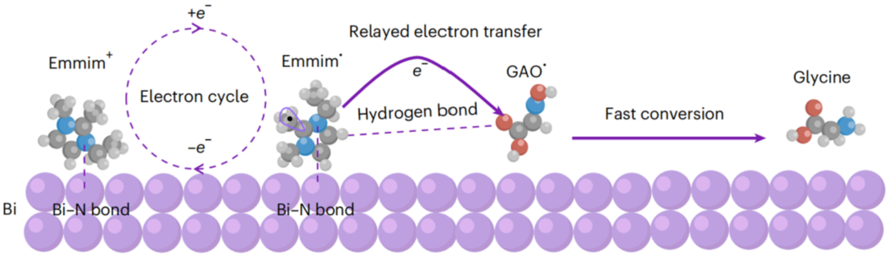

Figure 3. Schematic illustration of the relayed electron transfer mechanism for glycine electrosynthesis over IL@Bi catalyst. [Adapted from Ref. [2], copyright 2026, with permission from Springer Nature.]

The electrosynthesis of glycine from oxalic acid proceeds through three sequential steps: electrochemical reduction of oxalic acid to glyoxylic acid ($H_2C_2O_4+2H^++2e^-\rightarrow OHC\text{-}COOH$), nitrate reduction to NH_2OH ($NO_3^-+7H^++6e^-\rightarrow NH_2OH+2H_2O$), and spontaneous C–N coupling followed by electrocatalytic hydrogenation to yield glycine ($OHC\text{–}COOH+NH_2OH\rightarrow HO\text{-}N\text{=}CH\text{-}COOH+H_2O$, $HO\text{-}N\text{=}CH\text{-}COOH+4H+4e^-\rightarrow NH_2\text{-}CH_2\text{-}COOH+H_2O$). The susceptibility of NH_2OH to over-reduction and diffusive loss during this multi-step process represents the primary selectivity challenge. Here, bismuth-based catalysts modified with ionic liquids (IL@Bi) were designed to solve this problem via an electron relay mechanism shown in Figure 3. Ionic liquid-derived imidazolium radicals act as relay electron transfer mediators, accelerating electron delivery to surface-bound intermediates, shortening their residence time, and thereby suppressing decomposition and competing reduction pathways. This mechanism can effectively solve the problem of intermediate loss [2].

3. In situ characterization techniques

Traditional non in situ characterization can only capture static information after the reaction has completed, inherently missing the transient intermediates and dynamic surface processes that govern selectivity. In contrast, in situ characterization enables real-time, operando monitoring of the full catalytic cycle — from surface adsorption and interfacial charge transfer to bulk diffusion and product release — and has become indispensable for establishing mechanistic understanding of electrocatalytic NO_x-to-amino acid conversion.

Nevertheless, each individual technique carries intrinsic limitations that preclude a complete mechanistic picture on its own [11]. In situ infrared spectroscopy provides sensitive detection of adsorbed species at the electrode–electrolyte interface by monitoring characteristic vibrational modes of functional groups and chemical bonds. However, the spectra yield fingerprint-level information — the presence of a carbonyl stretch or N–H bending mode — rather than unambiguous molecular identities, and intermediate assignments therefore require corroborating evidence from complementary methods or isotope-labeling experiments [1]. In situ differential electrochemical mass spectrometry (DEMS) can detect soluble/volatile intermediates in real-time, providing kinetic information based on their mass-to-charge ratios (m/z), providing valuable kinetic information on product evolution. A critical limitation, however, is that a single m/z value can correspond to multiple species or molecular fragments: in glycine electrosynthesis, for example, m/z = 76 could in principle arise from glycine itself, from oxime intermediates, or from fragmentation of larger species, making unambiguous assignment impossible without independent structural confirmation [3]. In situ electron paramagnetic resonance (EPR) can directly capture free radical intermediates. Its fundamental limitation is selectivity: EPR is blind to EPR-inactive intermediates, which constitute the majority of closed-shell species (NH_2OH, oxime, imine) in the reaction network, and thus provides an inherently incomplete portrait of the cascade [5]. X-ray absorption spectroscopy (XAS) can analyze the electronic structure and active site coordination environment of catalysts. Synchrotron-based XAS offers sufficient photon flux for time-resolved measurements (millisecond timescales), whereas laboratory X-ray sources lack the intensity required to resolve transient structural changes. More fundamentally, the XAS signal represents an ensemble average over all absorbing atoms within the irradiated volume: surface-adsorbed reaction intermediates, which constitute only a small fraction of total metal atoms, contribute negligibly to the measured signal and are effectively undetectable [3]. In this respect, XAS is complementary to rather than competitive with surface-sensitive techniques such as infrared and Raman spectroscopy, which are better suited for tracking adsorbed intermediate evolution. It is therefore only through the deliberate combination of multiple in situ techniques — pairing the interface sensitivity of infrared spectroscopy with the kinetic resolution of DEMS, the radical detection capability of EPR, and the active-site structural insight of XAS — that the complete cascade reaction pathway from $NO_x \rightarrow NH_2OH \rightarrow$ oxime → amino acid can be reconstructed with direct experimental evidence [11].

3.1. Attenuated total reflection surface-enhanced infrared absorption spectroscopy (ATR-SEIRAS)

The following example illustrates how this multi-technique approach operates in practice. Although the mechanistic discussion below focuses on alanine electrosynthesis as a model system, the underlying cascade pathway — $NO_x \rightarrow NH_2OH \rightarrow$ oxime → amino acid— is directly analogous to that operative in glycine synthesis, differing only in the identity of the α-keto acid substrate (pyruvic acid versus glyoxylic acid). The reaction intermediates were tracked by potential-dependent in situ ATR-SEIRAS spectroscopy under three conditions: pure NO reduction, pure pyruvate (PA) reduction, and their co-reduction over oxidatively deposited silver (OD-Ag) (Figure 4). During pure NO electroreduction, a peak at 1195 cm^{-1} corresponding to surface-adsorbed NH_2OH appeared at

+0.34 V vs. RHE, alongside NH_4^+ bending doublets at 1451 and 1417 cm^{-1}. The appearance of $*NH_2OH$ at this relatively positive potential indicates that NO reduction occurs preferentially before other reactions. During PA reduction, characteristic peaks of the alcoholic hydroxyl group at 1330 cm^{-1} and a redshift of the C−O bond from 1215 to 1209 cm^{-1} emerged at −0.26 V, indicating lactic acid formation via PA hydrogenation. During co-reduction of NO and pyruvate, the NH_2OH signal fell below the detection limit, indicating its complete and rapid condensation with pyruvate. A C=N stretching band at 1666 cm^{-1} appeared at +0.04 V accompanied by attenuation of the C=O band at 1743 cm^{-1}, capturing the conversion from carbonyl and NH_2OH species to the pyruvate oxime intermediate. At −0.36 V, the emergence of a C−N stretching band at 1474 cm^{-1} confirmed the subsequent reductive amination from pyruvate oxime (C=N) to alanine (C−N). These results establish the full cascade NO → NH_2OH → pyruvate oxime → alanine pathway, and demonstrate that the close reduction potentials of PA and pyruvate oxime lead to competing lactic acid formation, accounting for the limited selectivity of the one-pot system.

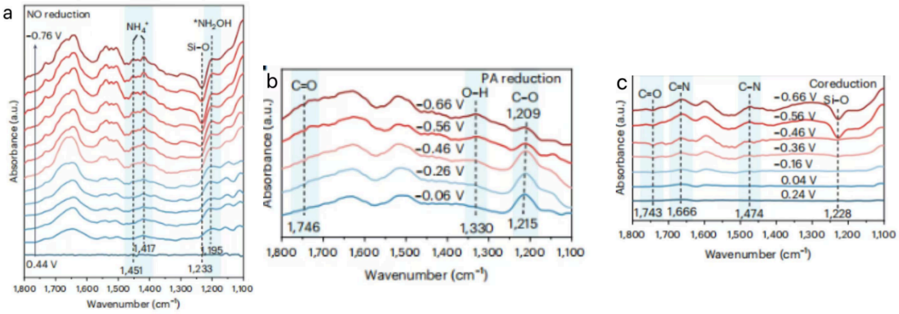

Figure 4. (a). In situ ATR- SEIRAS spectra of pure NO reduction over OD-Ag at different potentials; (b). In situ ATR- SEIRAS spectra of pure PA reduction over OD-Ag at different potentials; (c). In situ ATR- SEIRAS spectra of NO/PA co-reduction over OD-Ag at different potentials. [Adapted from Ref. [11], copyright 2023, with permission from Springer Nature.]

3.2. DEMS

DEMS, as a powerful in situ technique that directly couples an electrochemical cell with a mass spectrometer, is fundamentally distinct from conventional mass spectrometry (MS). Unlike conventional MS, which analyzes ex situ post-reaction electrolytes or gas products and provides only static snapshots of accumulated species, DEMS enables real-time, potential-resolved tracking of short-lived volatile/semi-volatile intermediates under working electrochemical conditions. This unique capability is critical for disentangling the complex cascade pathways in NO_x-to-amino acid electrosynthesis, which proceeds via NO_x → NH_2OH → oxime → amino acid.

The representative DEMS profiles for NO electroreduction and NO/α-keto acid coreduction are shown in Figure 5 (from Ref. [11]). Given that this work is highly representative and systematically elucidates the core mechanism of NO_x-to-amino acid electrosynthesis in Ref. [11], the relevant data and mechanistic insights are cited herein as typical examples. During pure NO electroreduction, a characteristic mass-to-charge signal at m/z = 33 (assigned to NH_2OH) emerges at relatively positive potentials and gradually intensifies with decreasing potential, directly confirming the formation of the key hydroxylamine intermediate. When α-keto acid is introduced for coreduction, the m/z = 33 signal of NH_2OH rapidly diminishes, while no new oxime signal is observed in the gas phase, indicating that in situ-generated NH_2OH spontaneously condenses with α-keto acid to form oxime at the electrode-electrolyte interface. This dynamic consumption of NH_2OH, uniquely captured by

DEMS, provides direct evidence for the rate-determining condensation step in the cascade pathway. In addition, DEMS can detect gaseous byproducts and track their formation, revealing the competing NO over-reduction pathway. This capability makes DEMS essential for distinguishing transient intermediates from stable products, supporting mechanistic understanding and catalyst design for NO_x-to-amino acid synthesis.

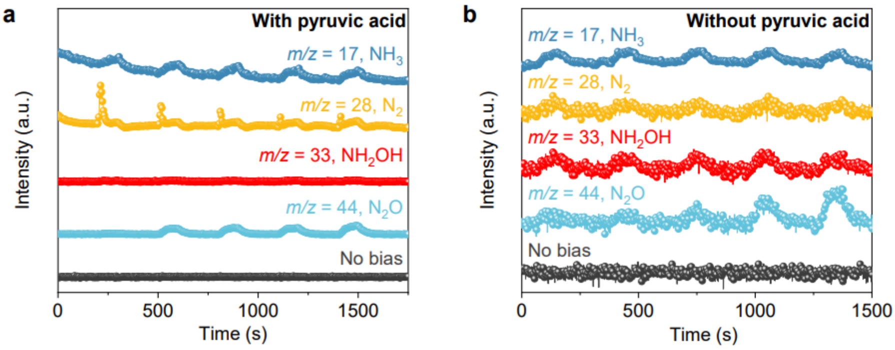

Figure 5. DEMS signals of key intermediates during NO reduction with/without pyruvic acid. The quenching of NH_2OH (m/z = 33) in (a) directly supports the stepwise C–N coupling pathway for amino acid synthesis. [Adapted from Ref. [11], copyright 2023, with permission from Springer Nature.]

3.3. EPR

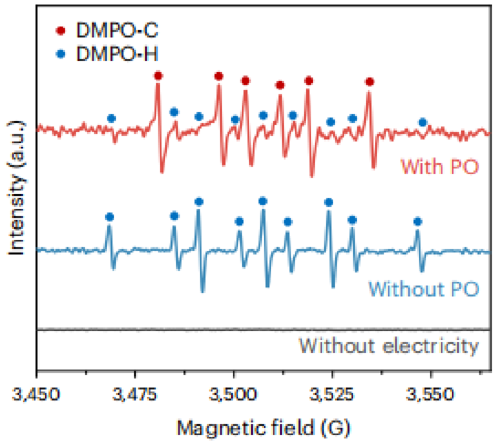

Figure 6. In situ EPR spectra showing that the DMPO-C radical signal appears only in the presence of pyruvic oxime (PO), confirming the formation of carbon-centered radicals during oxime hydrogenation. [Adapted from Ref. [11], copyright 2023, with permission from Springer Nature.]

In EPR spectroscopy enables direct capture of radical intermediates during electrocatalytic reactions, providing unique insights into radical-mediated elementary steps that are difficult to access by conventional methods. As discussed in the ATR-FTIR section, the electrosynthesis of alanine over OD-Ag proceeds via a cascade NO → hydroxylamine → pyruvate oxime (PO) → alanine pathway, in which the PO reduction step was identified as rate-limiting. To probe the radical nature of this step, quasi in situ EPR measurements were performed using DMPO as a spin-trapping agent (Figure 6). No obvious radical signals are detected on either OD-Ag or c-Ag NPs in the absence of PO, indicating that NO reduction alone rarely involves radicals. In the presence of PO, a characteristic six-line EPR signal (g = 2.0069, αN = 15.7, αH = 22.6) is clearly observed on OD-Ag, while no signal is detected on c-Ag NPs. This signal is assigned to the carbon-centered radical generated from pyruvate oxime hydrogenation. The in situ EPR results clearly reveal the radical evolution behavior during electrocatalysis and directly capture the carbon-centered radical intermediate from pyruvate oxime hydrogenation. By capturing radical intermediates in situ, EPR provides direct experimental evidence for elucidating electrocatalytic mechanisms and revealing the role of active sites, highlighting its unique advantages in resolving radical-mediated electrosynthesis pathways.

3.4. XAS

In situ XAS providing the critical dynamic information that conventional methods cannot capture. Conventional ex situ extended X-ray absorption fine structure (EXAFS), such as the spectra of OD-Ag, Ag foil, and c-Ag nanoparticles (NPs) shown in Figure 7 (adapted from Ref. [11]), only reveals the static coordination environment of the catalyst before the reaction. The experimental data and fitting curves in both k-space (left panels) and R-space (right panels) clearly show that OD-Ag has a unique Ag–Ag coordination structure compared to its bulk and nanoparticle counterparts, confirming its distinct structural features [11]. However, these static measurements cannot track how the local coordination evolves under electrochemical conditions.

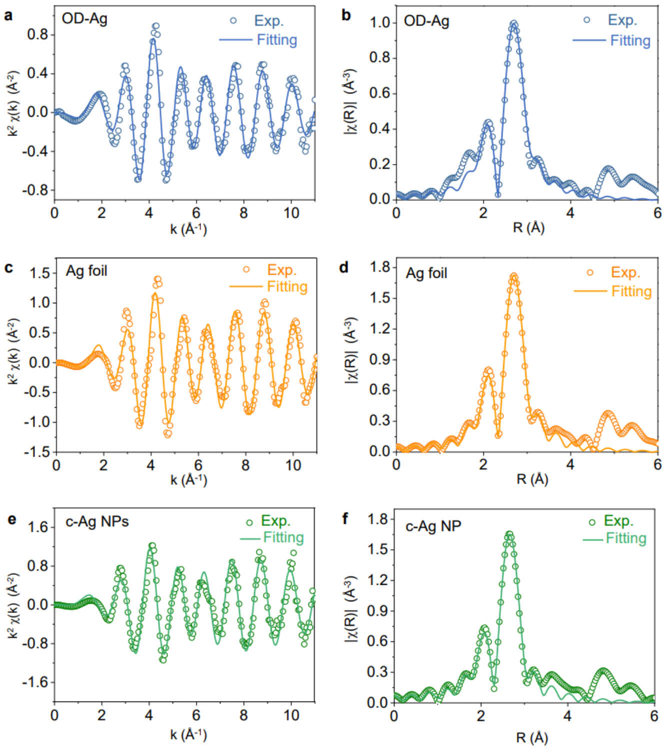

Figure 7. The spectra confirm that OD-Ag is fully reduced to metallic Ag, with no Ag-O coordination observed. Adapted from Ref. [11], copyright 2023, with permission from Springer Nature.

In situ XAS enables real-time monitoring of the catalyst's electronic state and coordination environment under working conditions, directly linking structural evolution to reaction activity. The mechanistic study of NO electroreduction over AD-Fe/NC by Xian et al. provides a representative example of its application in electrocatalytic amino acid synthesis (Figure 8). Potential-dependent Fe K-edge X-ray Absorption Near-Edge Structure (XANES) spectra reveal a low-energy shift of the white-line peak as the potential decreases from ex situ to −0.2 V vs. RHE, indicating partial reduction of Fe(III) centers that facilitates adsorption of reactive nitrogen species. Further decrease to −0.6 V increases the white-line peak intensity, consistent with NO accumulation at the Fe sites, while subsequent decrease to −1.0 V attenuates the peak, providing direct evidence that reductive amination proceeds efficiently at this potential. Notably, strong NO adsorption is retained upon returning to open-circuit voltage, confirming the structural robustness of the Fe single-atom sites. At the local structural level, in situ EXAFS fitting reveals that at −0.6 V, an additional Fe–N scattering path at 2.11 Å emerges alongside the original four-coordinate Fe–N bonds (2.07 Å), attributed to NO adsorbed on the Fe sites. At −1.0 V, the retained Fe–N coordination is ascribed to chemical binding with the NH_2OH intermediate during reductive amination. Together, these potential-resolved in situ EXAFS results establish atomic-level evidence for the sequential NO adsorption, NH_2OH formation, and C–N coupling steps underlying electrocatalytic amino acid synthesis.

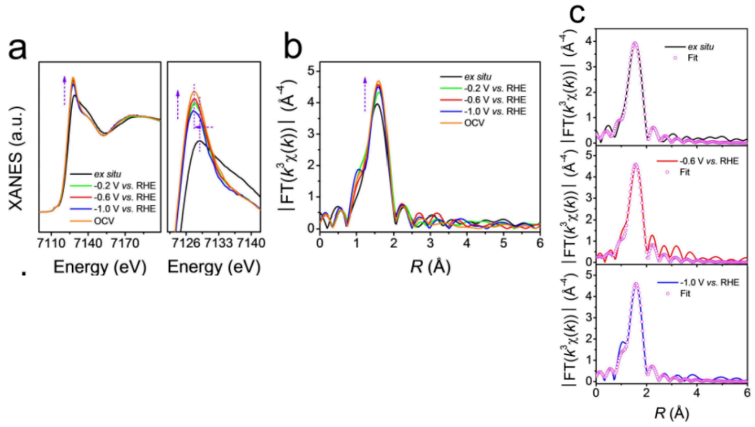

Figure 8. In situ XAS characterization of the Fe-N-C catalyst during NO electroreduction. (a) Fe K-edge in situ XANES spectra at different potentials; (b) k3-weighted EXAFS spectra; (c) EXAFS fitting results. [Adapted from Ref. [4], copyright 2023, with permission from the publisher.]

4. Conclusion and perspectives

Taking glycine electrosynthesis as a representative case, this review systematically summarizes the research progress on the mechanism of electrocatalytic NO_x conversion to amino acids. Regardless of whether glyoxylic acid is supplied directly or generated in situ from oxalic acid, the reaction follows a unified cascade pathway: NO_x → hydroxylamine → oxime → amino acid. The selective generation and stabilization of hydroxylamine directly determine the selectivity and efficiency of the reaction. Catalyst design strategies across different systems, from bimetallic alloys and single-atom sites to ionic liquid mediators, converge on the same mechanistic imperative: suppressing over-reduction of hydroxylamine while promoting its efficient C−N coupling. In situ characterizations exhibit strong complementarity: ATR-SEIRAS identifies adsorbed interfacial species, DEMS monitors dynamic consumption of gaseous or volatile intermediates, EPR detects radical pathways, and XAS unravels electronic/structural evolution of active sites. Their synergistic integration enables comprehensive reconstruction of the full electrocatalytic mechanism.

Current research on the electrocatalytic conversion of nitrogen oxides to amino acids has advanced rapidly in mechanistic analysis and catalyst development. However, several key challenges remain before practical applications. Most existing studies rely on simplified model systems with single nitrogen and carbon sources. In real exhaust gas and wastewater, multiple nitrogen oxides coexist, and their competitive reaction pathways remain unclear, limiting practical relevance. Whether C−N coupling occurs spontaneously in solution or is catalyzed at the electrode surface still lacks direct experimental evidence, hindering precise regulation of reaction pathways. In catalyst design and selection, the Faradaic efficiency and yield still leave much room for improvement. Rational design of bifunctional catalysts that simultaneously optimize hydroxylamine generation and C−N coupling represents a promising direction. Furthermore, scaling from laboratory H-cells to flow cells is critical for commercialization, yet related research and practical implementation are insufficient, forming a major bottleneck for industrialization. Existing characterization techniques lack time resolution needed to capture transient intermediates on the millisecond timescale relevant to electrode kinetics.

Looking further ahead, beyond relying solely on fossil-derived feedstocks, the integration of renewable carbon resources, such as biomass-derived oxalic acid or glyoxylic acid, holds great promise for sustainable glycine production [12]. Furthermore, coupling electrocatalysis with plasma-activated NO_x technology [13] enables a full-chain, low-energy green synthesis of amino acids from nitrogen, achieving efficient nitrogen resource utilization. Integration with intermittent renewable energy such as solar power would build a truly zero-carbon amino acid synthesis route, aligning with sustainable development goals [14]. Realizing this vision requires coordinated advances across catalyst design, reactor engineering, and system integration [15], but the mechanistic foundation established by the studies reviewed here provides a solid basis for that next step.

References

[1] Cheng, Y. et al. (2024) Highly Efficient Electrosynthesis of Glycine over an Atomically Dispersed Iron Catalyst. Journal of the American Chemical Society, 146(14), 10084-10092.

[2] Wang, H. et al. (2026) Imidazolium radical-mediated electron transfer enhances electrochemical C–N coupling for glycine synthesis. Nature Synthesis, 5(1), 74-83.

[3] Xian, J., Li, S., Su, H., Liao, P., Wang, S., Xiang, R., Zhang, Y., Liu, Q., and Li, G. (2023) Electrosynthesis of α-Amino Acids from NO and other NO_x species over CoFe alloy-decorated Self-standing Carbon Fiber Membranes. Angewandte Chemie, 62(30), e202306726.

[4] Xian, J. et al. (2023) Electrocatalytic Synthesis of Essential Amino Acids from Nitric Oxide Using Atomically Dispersed Fe on N-doped Carbon. Angewandte Chemie, 62(26), e202304007.

[5] Wang, Y. et al. (2025) Proton-Regulated C–N Coupling for Efficient Amino Acid Electrosynthesis. Journal of the American Chemical Society, 147(51), 47370-47380.

[6] Hermawan, A., Alviani, V.N., Wibisono, and Seh, Z.W. (2023) Fundamentals, rational catalyst design, and remaining challenges in electrochemical NO_x reduction reaction. iScience, 26(8), 107410.

[7] Udayasurian, S.R., and Li, T. (2024) Recent research progress on building C–N bonds via electrochemical NO_x reduction. Nanoscale, 16(6), 2805-2819.

[8] Kim, J.E., Jang, J.H., Lee, K.M., Balamurugan, M., Jo, Y.I., Lee, M.Y., Choi, S., Im, S.W., and Nam, K.T. (2021) Electrochemical Synthesis of Glycine from Oxalic Acid and Nitrate. Angewandte Chemie, 60(40), 21943-21951.

[9] Xian, J., Cai, K., Liao, P., Wang, S., and Li, G. (2024) Upgrading waste NO_x into amino acids viaelectrocatalysis on Co nanoparticles encapsulated in hollow carbon nanofibers. Science China Chemistry, 67(6), 1946-1952.

[10] Zhou, W. et al. (2025) Highly Selective Electrosynthesis of Glycine from Glyoxylic Acid and Nitrate via Stabilizing the NH2OH Intermediates. Angewandte Chemie, 65(3), e16749.

[11] Li, M., Wu, Y., Zhao, B.-H., Cheng, C., Zhao, J., Liu, C., and Zhang, B. (2023) Electrosynthesis of amino acids from NO and α-keto acids using two decoupled flow reactors. Nature Catalysis, 6(10), 906-915.

[12] Ding, M., Song, S., and Li, X. (2024) A perspective on renewable production of amino acids from biomass through the chemocatalytic method. Green Chemistry, 26(8), 4468-4476.
[13] Wu, S., and Liu, F. (2025) Recent Progress in the Electrochemical Formation of C−N Bonds for Construction of Organic Compounds via the Use of NO_x/NO_x^-. ChemSusChem, 18(4), e202401751.
[14] Zhang, X., Lyu, Y., Ding, J.J., Wang, X., Johannessen, B., Jiang, S.P., and Zheng, J. (2025) Using waste CO_2 to produce essential amino acids for humans: An efficient photoelectrochemical route. Science Advances, 11(12), eadr8651.
[15] Liu, X., Liao, P., Liao, W., Wang, S., and Li, G. (2025) Research progress of coordination materials for electrocatalytic nitrogen oxides species conversion into high-value chemicals. EnergyChem, 7(2), 100146.