

Review

Research Progress of Electrocatalysts for N₂ Reduction to NH₃ Under Ambient Conditions

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Abstract

Ammonia is an ideal candidate for clean energy in the future, and its large-scale production has long relied on the Haber–Bosch process, which operates at a high temperature and pressure. However, this process faces significant challenges due to the growing demand for ammonia and the increasing need for environmental protection. The high energy consumption and substantial CO₂ emissions associated with the Haber–Bosch method have greatly limited its application. Consequently, increasing research efforts have been devoted to developing green ammonia synthesis technologies. Among these, the electrocatalytic nitrogen reduction reaction (NRR), which uses water and nitrogen as raw materials to synthesize NH₃ under mild conditions, has emerged as a promising alternative. This method offers the potential for carbon neutrality and decentralized production when coupled with renewable electricity. However, it is important to note that the current energy efficiency and ammonia production rates of NRR under ambient aqueous conditions generally lag behind those of modern Haber–Bosch processes integrated with green hydrogen (H₂). As the core of the NRR process, the performance of electrocatalysts directly impacts the efficiency, energy consumption, and product selectivity of the entire reaction. To date, significant efforts have been made to identify the most suitable electrocatalysts. In this paper, we focus on the current research status of metal catalysts—including both precious and non-precious metals—as well as non-metal catalysts. We systematically review important advances in performance optimization, innovative design strategies, and mechanistic analyses of various catalysts. We clarify innovative optimization strategies for different catalysts and summarize and compare the catalytic effects of various catalyst types. Finally, we discuss the challenges facing electrocatalysis research and propose possible future development directions. Through this paper, we aim to provide guidance for the preparation of high-efficiency NRR catalysts and the future industrial application of electrochemical ammonia synthesis.

Keywords: electrocatalyst; NRR; optimal mechanism; competitive reaction; ammonia



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1. Introduction

With the continuous consumption of traditional fossil fuels, environmental pollution and greenhouse gas emissions are becoming increasingly severe [1–3]. Mankind is facing

unprecedented energy shortages and ecological deterioration. In this context, it is imperative to develop a new clean energy system. Ammonia (NH_3) can serve as a potential zero carbon energy carrier due to its zero carbon emissions, high energy density, and ease of liquefaction [4], aligning with the strategic goals of carbon peaking and carbon neutrality. Additionally, ammonia, as the basic raw material in the industrial sector, has an annual production exceeding 200 million tons and is widely used in the synthesis and manufacture of fibers, dyes, refrigerants, and other products [5]. In addition, 82.3% of the ammonia molecule consists of nitrogen, which is the primary raw material for synthetic fertilizers, such as urea and ammonium nitrate [6,7]. This makes ammonia the “source of life” for modern agriculture, and more than 70% of the world’s nitrogen fertilizer production depends on ammonia as a key raw material, supporting the food supply for over half of the global population. Therefore, advancing the ammonia synthesis process holds significant potential for sustainable human development.

Currently, the most widely used ammonia synthesis technology worldwide is the Haber–Bosch process, developed in the 20th century and driven by fossil fuels. This process requires a high temperature environment of 300–500 °C and pressures of 15–30 MPa [8–10], as well as iron-based or ruthenium-based catalysts to convert high-purity nitrogen and hydrogen into ammonia through thermal catalysis. Although the Haber–Bosch process remains the most mature method for NH_3 synthesis, producing approximately 170 million tons annually [2], it demands substantial energy input under high temperature and pressure conditions, and is accompanied by a large amount of carbon dioxide (CO_2) emissions, and its carbon emissions scale poses a major challenge to global climate governance. In addition, the process suffers from low energy efficiency. Given the increasing global demand for ammonia to support a growing population, there is an urgent need for a new, efficient, and environmentally friendly ammonia synthesis method.

In recent years, to actively support the national green and sustainable development strategy, many researchers have developed a variety of green, low-carbon, and environmentally friendly synthetic ammonia technologies that can replace the Haber–Bosch process, such as photocatalytic ammonia synthesis, electrocatalytic ammonia synthesis, and biological nitrogen fixation [11–13], as illustrated in Figure 1. Biological nitrogen fixation in nature is carried out by metallonitrogenases with Fe–Mo, Fe–V, or Fe–Fe active sites under mild conditions, with Fe–Mo being the most active and abundant enzyme for reducing N_2 [14]. Metal nitrogenase essentially functions as a homogeneous enzymatic catalytic system, but its structural characteristics are very similar to the Mo–Fe–S system in the non-catalytic system, and the catalytic mechanism provides a low-potential, multi-electron transfer environment for the reaction system. Although biological nitrogen fixation is environmentally friendly and sustainable, although it has the advantages of being environmentally friendly and sustainable, its ammonia production is currently low and cannot meet present or future demand for NH_3 [15], which is due to the fact that biological nitrogen fixation occurs only in a select group of microorganisms, and nitrogenase exhibits poor stability and is easily inactivated by oxygen. Photocatalytic ammonia synthesis is a green technology that uses light energy to drive the reaction between nitrogen and water to produce ammonia, which absorbs light energy through semiconductor photocatalysts to generate electron–hole pairs, which trigger the reduction of nitrogen and the oxidation of water, and finally realizes the synthesis of ammonia, but due to low light utilization efficiency, low active site density, and the rapid recombination of photoexcited electron–hole pairs [16,17]. The conversion efficiency of solar energy to chemical energy remains unsatisfactory. Electrocatalytic ammonia synthesis was first demonstrated in 1807 by Humphrey Davy and has since been extensively studied. This technology operates under mild reaction conditions, provides the required electrical energy through renewable energy sources (such as solar energy, wind

energy, tidal energy, etc.) to drive the reaction of nitrogen (N_2) and hydrogen ions (H^+) on the surface of the catalyst to produce ammonia (NH_3), has a higher energy efficiency than the Haber–Bosch process, and allows flexible control of the reaction by adjusting external parameters (such as electrochemical voltage, electrolyte pH, etc.) to achieve high ammonia yields. Additionally, it facilitates modularization and small-scale operations, and at the same time, NRR reactions can also promote the activation of nitrogen molecules through electrical energy, overcoming thermodynamic limitations [18,19]. The purpose of green ammonia synthesis is to utilize renewable energy and water to replace the Haber–Bosch method under mild conditions, and carries out the scientific rationale for the chemical storage and transportation of renewable electricity in the form of ammonia by enabling the activation and transformation of N_2 molecules under mild conditions. Therefore, electrocatalytic ammonia synthesis technology supports the achievement of the sustainable development strategy and the realization of carbon neutrality and carbon peak goals, and can be used as an excellent strategy to replace the Haber–Bosch process for ammonia production.

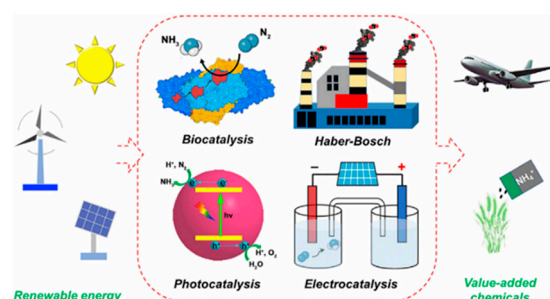


Figure 1. Schematic diagram of nitrogen fixation processes, including biological, industrial, photocatalytic, and electrocatalytic ammonia synthesis.

In recent years, although significant progress has been made in electrocatalytic NRR ammonia synthesis technology, the dissociation of nitrogen remains challenging due to the strong $\text{N}\equiv\text{N}$ bond energy, and the strong competitive hydrogen evolution reaction (HER) throughout the process results in a low ammonia yield from NRR [20,21]. Catalysts play a crucial role in determining the selectivity, efficiency, and energy consumption levels of electrocatalytic NRR. In order to efficiently and selectively convert N_2 to NH_3 under mild conditions, it is essential to select or design electrocatalysts with low energy barriers, high selectivity, and thermal stability. In a previously published journal article, the researchers extensively investigated the NRR mechanism and sought to develop efficient electrocatalysts. This review provides an overview and concise analysis of the current research on the properties of common NRR electrocatalysts and strategies for their optimization.

Previous reviews have predominantly focused on the research progress concerning specific catalyst categories, such as defect-engineered catalysts (focusing on mechanisms and design), as well as the performance and advancements of various catalytic reactions involving transition metal phosphides (TMPs), metal-free catalysts (MFCs), and specific M–N–C-based catalysts. However, a comprehensive summary and comparative analysis of the application efficacy and industrial potential across different catalyst metal types is still lacking.

This review highlights the recent advances in the electrochemical NRR for ammonia (NH_3) synthesis. We consolidate key developments involving precious metal, non-precious metal, and defect-engineered non-metallic catalysts, with a particular focus on performance improvements, innovative design strategies, and mechanistic insights. By integrating specific experimental case studies with density functional theory (DFT) calculations and in situ characterization techniques, we elucidate quantitative structure–activity relationships, advancing a mechanistic understanding from hypothesis to verification. To clarify the optimization pathways previously noted as ambiguous, we propose the following concrete

strategies: for precious metals, cost reduction and stability enhancement can be achieved through single-atom dispersion and carrier modification; for non-precious metals, bimetallic synergy offers a promising approach to improve Faradaic efficiency; and for non-metals, precise heteroatom doping provides a means to overcome activity bottlenecks.

In summary, this review provides a comprehensive overview of the current research in the field of electrocatalytic nitrogen reduction and outlines clear strategies for catalyst optimization.

2. Development of High-Efficiency NRR Catalysts

The catalyst is the most critical factor determining the performance of the NRR. NRR catalysts should exhibit high NH_3 yields and Faradaic efficiency, excellent selectivity and long-term stability, as well as mechanical and thermodynamic stability. Currently, numerous researchers worldwide are dedicated to studying efficient electrocatalysts for N_2 reduction, elucidating the specific reaction mechanism of N_2 reduction, and trying to make applicable electrocatalysts. These catalysts can be broadly categorized into non-metallic electrocatalysts and metallic electrocatalysts based on their metal content. Due to their unique electronic structures and surface properties, these materials demonstrate promising potential for NRR applications.

2.1. Metal Catalysts

Metal materials are commonly used as electrocatalysts due to their active properties and excellent electrical conductivity. Based on the cost of the metals used in catalysts, they can be subdivided into precious metal catalysts and non-precious metal catalysts.

2.1.1. Precious Metal Catalysts

As a prominent research hotspot in the field of electrocatalytic ammonia synthesis, precious metal catalysts have shown significant potential in the activation and reduction of nitrogen due to their unique electronic structures and excellent catalytic activity. Among them, precious metals include eight metal elements, gold, silver, ruthenium, rhodium, palladium, osmium, iridium, and platinum [22–24], and the precious metals possess unfilled d orbitals, enabling the efficient adsorption and activation of the inert $\text{N}\equiv\text{N}$ triple bond, thereby facilitating the conversion of nitrogen to ammonia by lowering the reaction energy barrier. For example, ruthenium-based catalysts are considered one of the ideal candidates for NRR due to their moderate bond strength with nitrogen molecules, and their single-atom dispersed form can significantly enhance the atomic utilization and reduce the required amount of precious metals. Additionally, precious metal catalysts exhibit strong resistance to poisoning and can tolerate the influence of trace impurities (such as CO , H_2S) in the reaction system, which helps maintain long-term catalytic activity.

The experimental results of Hao et al. [25] showed that N_2 could be electrochemically reduced to NH_3 at an isolated Pt site on WO_3 nanoplates, and exhibited the highest electrochemical NH_3 yield at -0.2 V vs. RHE potential in a 0.1 M K_2SO_4 neutral solution (Figure 2c) ($342.4 \mu\text{g h}^{-1} \text{mg}^{-1}_{\text{Pt}}$) and a Faradaic efficiency of 31.1%, which are approximately 11- and 15-times higher, respectively, than their nanoparticle counterparts. Mechanistic analysis showed (Figure 2d) that the conversion of N_2 to NH_3 followed an alternating hydrogenation pathway, and DFT calculations and in situ FT-IR yielded positively charged isolated Pt sites with a unique Pt-3O structure that favorably adsorbs and activate N_2 . In addition, the hydrogen evolution reaction is significantly suppressed on the WO_3 nanoplate modified with isolated Pt site; specifically, the electron-rich Pt tends to adsorb H atoms, and the number of adsorbed H atoms correlates positively with HER activity. In contrast, isolated Pt atoms are usually coordinated with atoms such as O and

N, which anchor Pt to make it more electron-deficient and therefore less susceptible to the adsorption of H atoms and attack by N₂.

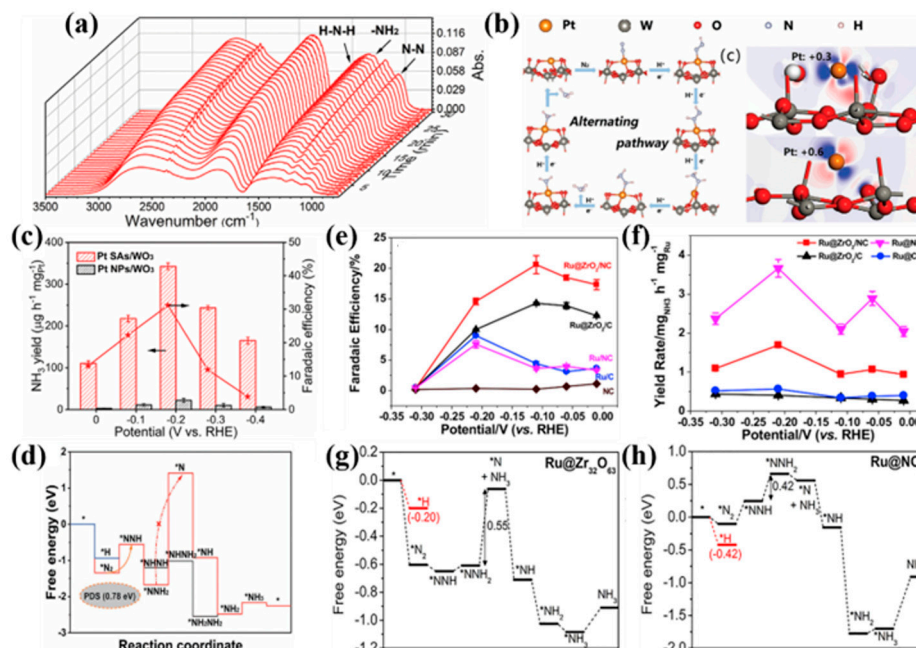


Figure 2. (a) Electrochemical in situ time-resolved FTIR spectra of the nitrogen reduction reaction on the Pt SAs/WO₃ electrode [25]; (b) representative alternate pathways of N₂ reduction on the Pt-3O structure [25]; (c) NH₃ yield and Faradaic efficiency of Pt SAs/WO₃ and Pt NPs/WO₃ at 0.1 M K₂SO₄ [25]; (d) free energy step diagram of the nitrogen reduction reaction at isolated Pt sites with a Pt-3O structure at U = 0 V [25]; (e,f) FE and NH₃ yields of Ru@NC, Ru@C, Ru@ZrO₂/NC, and Ru@ZrO₂/C at each applied potential [26]; (g,h) NRR free energy step plots for Ru@Zr₃₂O₆₃ and Ru@NC₂ (* The symbol is used to indicate the intermediates adsorbed on the surface of the catalyst) [26].

Tao et al. [26] synthesized Ru@ZrO₂/NC by the pyrolysis of Zirconium (Zr)-based MOF (UiO-66) supported by Ru, and then used hydrofluoric acid (HF) to remove ZrO₂ particles, thereby obtaining a nitrogen-doped carbon-supported single-atom Ru catalyst (Ru/NC). As shown in Figure 2e,f, the NH₃ yield is 3.665 mg·h^{−1}·mg_{Ru}^{−1} at −0.21 V vs. RHE. The presence of ZrO₂ significantly inhibited the competitive hydrogen evolution reaction, and the Faradaic efficiency (FE) of Ru@ZrO₂/NC at −0.17 V vs. RHE potential was as high as 21%, surpassing that of most reported NRR catalysts. DFT calculations indicate that the hydrogenation reduction reaction of N₂ primarily occurs at the Ru metal site with an O vacancy, and its high catalytic performance is attributed to the stabilization of *NNH (* The symbol is used to indicate the intermediates adsorbed on the surface of the catalyst) intermediates, the pronounced instability of *H species, and the enhanced adsorption of N₂.

However, the commercial application of precious metal catalysts still faces significant challenges. First, the scarcity and high cost of precious metals result in expensive catalysts, making it difficult to meet large-scale industrial demands [27]. Secondly, the stability of precious metal catalysts under strongly alkaline conditions is insufficient, and they are prone to dissolution or agglomeration, which limits their application range. In addition, the competition from the hydrogen evolution reaction (HER) during the nitrogen reduction reaction hinders the Faradaic efficiency, representing a key bottleneck that restricts the performance of precious metal catalysts.

To overcome these limitations, the current research focuses on single-atom catalyst design (e.g., Ru@NC), auxiliary modulation (e.g., ZrO₂ to suppress HER), and synergistic

catalysis with non-precious metal materials. While reducing the overpotential to achieve an active benchmark, cost and performance are balanced through alloying, core-shell structure, and low catalyst loading. By guiding the material design with theoretical calculations, it is expected that the amount of precious metals can be reduced while improving the catalytic efficiency. In the future, the development of low-cost, highly active precious metal-based composite catalysts, the reduction of loading, the improvement of atomic utilization, or the exploration of new non-precious metal alternatives will be key directions to advance the practical application of NRR technology.

2.1.2. Non-Precious Metal Catalysts

Compared to precious metal catalysts, non-precious metal catalysts offer significant cost advantages and are more abundant in resources. These non-precious metals also have electron distributions or unoccupied orbitals similar to those of precious metals, enabling them to form coordination bonds that participate effectively in the reaction, and exhibit excellent NRR activity in numerous experimental studies, particularly metals such as iron (Fe), copper (Cu), nickel (Ni), cobalt (Co), and molybdenum (Mo) [28–31], which have garnered considerable attention because of their extensive research in this field.

Seong et al. [32] synthesized MoS₂ nanostructured materials doped with Fe, Ni, and Co (FeMoS₂, NiMoS₂, and CoMoS₂) by the hydrothermal method as catalysts for electrochemical nitrogen reduction reactions and evaluated their catalytic performance. As shown in Figure 3a–c, FeMoS₂/CC exhibits a relatively high NH₃ production rate of 2.74 µg h^{−1} mg^{−1} (equivalent to 7.81 µg h^{−1} cm^{−2}), with a Faradaic efficiency of 0.15%. Additionally, Figure 3d–f presents a comparative analysis of the catalyst's physicochemical properties before and after NRR, demonstrating that the transition of Mo and Fe to a higher oxidation state improves the initial N₂ adsorption and catalytic activity.

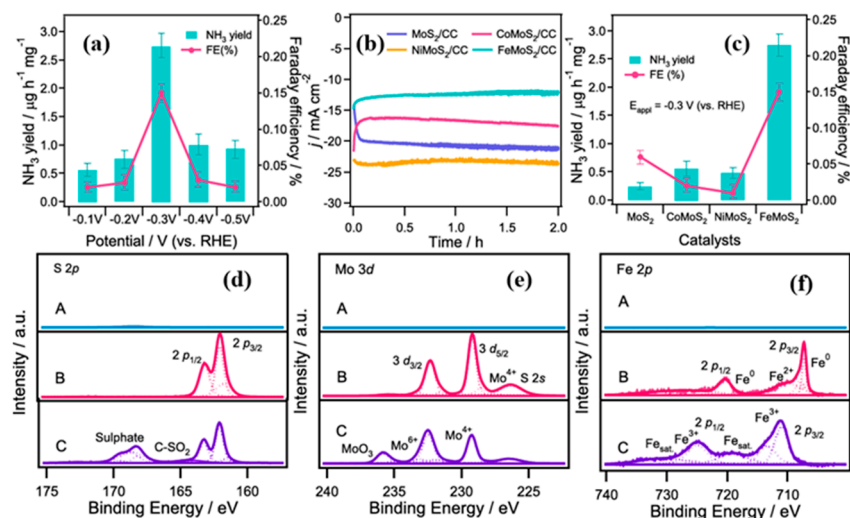


Figure 3. (a) NH₃ yield and FE of FeMoS₂/CC at different voltages [32]; (b) comparison of current density at −0.3 V vs. RHE for MoS₂/CC, CoMoS₂/CC, NiMoS₂/CC, and FeMoS₂/CC [32]; (c) NH₃ yield and FE measured at −0.3 V vs. RHE for MoS₂/CC, CoMoS₂/CC, NiMoS₂/CC, and FeMoS₂/CC [32]; (d–f) XPS analysis of electrode surface changes during 2 h NRR [32]: (d) CC, (e) FeMoS₂/CC before NRR, and (f) FeMoS₂/CC after NRR.

As shown in Figure 4a–d, Tang [33] investigated eight vanadium (V)-anchored sulfur (S)-doped graphene catalysts (V-S_xC_{Nc-x}@Gr) to study their NRR catalytic performance. V-S₂C@Gr exhibits excellent activity with a limiting potential of −0.17 V, outstanding thermodynamic and electrochemical stability, and good selectivity. Surprisingly, V-S₃@Gr outperforms V-S₂C@Gr, and the NRR on V-S₃@Gr is an exothermic process that contin-

uously reduces Gibbs free energy. NRR can occur spontaneously without an externally applied potential, and doping more S in the coordination environment of V leads to greater charge accumulation around V, resulting in a more efficient activation of $\text{N}\equiv\text{N}$ bonds, and ultimately a lower limiting potential. Lu [34] used holly leaves as a reducing agent to co-reduce copper and silver precursors, producing efficient and stable NRR electrocatalysts. From Figures 2 and 3f, it can be concluded that Cu_3Ag bimetallic nanosheets exhibit an excellent NRR performance at -0.2 V vs. RHE, with an NH_3 productivity of $31.3 \mu\text{g h}^{-1} \text{mg}^{-1} \text{cat}$, and a Faradaic efficiency of 31.3%. According to density functional theory (DFT) calculations, the excellent performance of Cu_3Ag bimetallic nanosheets may be attributed to Ag optimizing the 3d orbital occupancy of Cu and synergistically enhances the charge transfer during NRR (Figure 4e), resulting in intermediates with a suitable adsorption strength.

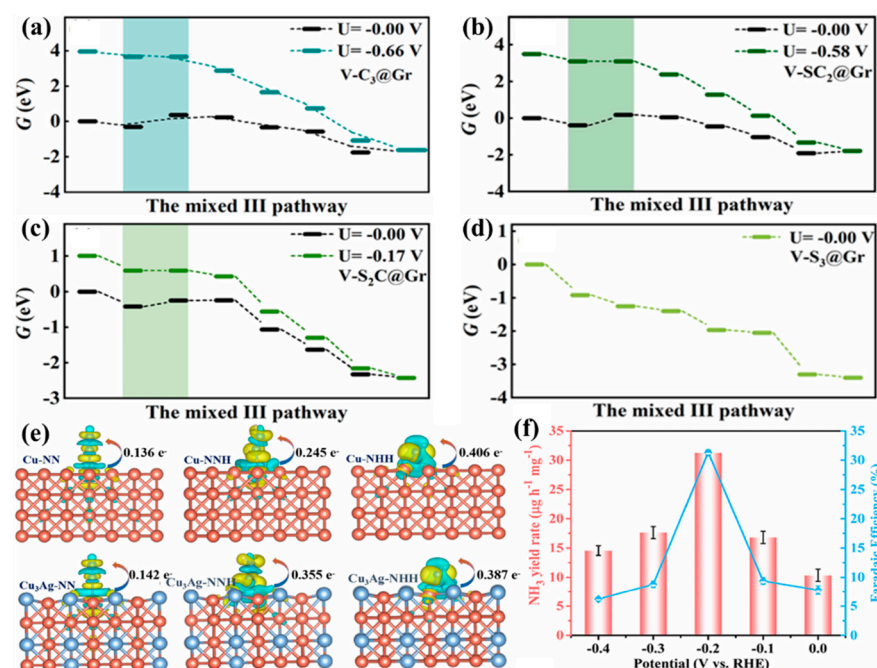


Figure 4. (a–d) Gibbs free energy step diagram of NRR on $\text{V-S}_x\text{C}_{3-x}\text{@Gr}$ [33]; (e) charge density difference and Bader charge analysis of N_2 , NNH , and NHH adsorbed on Cu and Cu_3Ag , where yellow represents electron density accumulation, blue represents electron density dissipation, and red, brown, blue, and white balls represent Ag, Cu, N, and H atoms, respectively [34]; (f) corresponding NH_3 yields and FE of Cu_3Ag bimetallic NSs [34].

Through a triple regulation strategy involving metal combination, coordination environment, and carrier coordination, non-precious metal catalysts can achieve activity, selectivity, and stability comparable to precious metal systems, providing a feasible path for the industrialization of green ammonia synthesis. Xiao et al. [1] compared the NRR paths of FeMo diatomic catalysts in two coordination structures (FeMo@NG-4N and 3N) and proposed site-selective regulation by substituting sulfur atoms for nitrogen atoms. Through electronic structure analysis, it was revealed that the introduction of S lowered the metal d-band center and adjusted the oxidation state of Mo to be in a moderate range, thereby optimizing the adsorption strength of intermediates. This breakthrough overcame the traditional bottleneck of adsorption being either too strong or too weak and demonstrated the HER inhibition ability and thermal stability of DAC under acidic conditions. The efficient activation of N_2 is achieved by breaking the scaling relationship typical of single-atom catalysts through electron complementarity between different metals. Xiong et al. [35,36], using g-CN as the carrier, found that the overpotential of the enzymatic

pathway of MoMn@g-CN was as low as 0.10 V, which filled the performance gap of g-CN-based DAC in the field of NRR. The 4d orbital of Mo accepts the σ electrons of N_2 , while the 3d orbital of Mn feeds back the electron to the π^* antibonding orbital of N_2 , synergistically weakening the $N\equiv N$ triple bond, and the bond length is extended from 1.114 Å to 1.197 Å. A comparison of the PDOS of single-atom catalysts Mo@g-CN and Mn@g-CN confirmed that the orbital hybridization in the bimetallic system is significantly stronger than that of single metal, highlighting the synergistic advantage of heteronuclear DAC.

Due to the reactive chemical properties for metals, the energy barrier of the electrocatalytic nitrogen reduction reaction is low, requiring only a small applied potential to drive the reaction. However, at the same time, the hydrogen evolution reaction competes strongly, resulting in a lower Faradaic efficiency for the target product NH_3 that is weaker than that of other types of catalysts. Compared to precious metal catalysts, non-precious metal catalysts exhibit a significantly higher Faradaic efficiency, and their activity can be significantly enhanced by single-atom or double-atom engineering. The d-band center is optimized via electron coupling effects between metals, balancing the N_2 adsorption and NH_3 desorption. The NH_3 yield of non-precious metal catalysts can reach 60%–80% of that of precious metals. Some high-performance non-precious metal catalysts achieve a Faradaic efficiency exceeding 90%, with catalytic yields approaching those of ammonia produced by the Haber–Bosch process. In addition, non-precious metal catalysts are abundant in source and low in price, and have great development potential, but non-precious metal catalysts are prone to agglomeration during the reaction [37], and their performance can be improved by modifying the catalyst. The stability of non-precious metals still needs to be improved by strong metals—support interactions are needed to enhance durability, as most catalysts exhibit low activity retention after 50 hours of continuous reaction. In general, non-precious metal catalysts are promising NRR catalysts, and if the impressed potential can be further reduced, it is possible to achieve large-scale applications in the future.

2.2. Non-Metallic Catalysts

Non-metallic catalysts primarily include carbon-based, boron-based, and phosphorus-based catalysts [38], among which carbon-based catalysts are the most common non-metallic catalysts, which are conducive to exposing more active sites and provide abundant channels for proton and electron transport due to their porous structure and large specific surface area. So far, the reported carbon-based materials mainly include graphene, activated carbon, carbon nanofibers, carbon nanotubes, biomass-derived carbon, and metal organic framework (MOF)-derived carbon materials. Additionally, non-metallic catalysts have a wide range of sources, are cost-effective, and exhibit a stable performance, making them extensively used in electrochemical NRR, CO_2 RR, ORR, NORR, etc. [39]. For example, in the field of fuel cells, non-metallic catalysts serve as alternatives to platinum-based materials by enhancing catalytic activity through doping or defect engineering, thereby reducing the reliance on scarce precious metals. In the carbon dioxide cycloaddition reaction, biofunctional organoboron catalysts demonstrate activity comparable to conventional metal catalysts and are recyclable. Furthermore, carbon-based non-metallic catalysts form multi-component active centers through doping with nitrogen, sulfur, and other elements, which exhibit high activity and long-lasting stability in the catalytic process of oxygen reduction, oxygen evolution, and hydrogen evolution, providing a low-cost solution for energy devices such as metal air batteries and water electrolysis systems.

Sun et al. [40] proposed a method for the preparation of homogeneous ternary boron nitride (BCN) nanosheets via the pyrolysis of organic–inorganic hybrid precursors. As shown in Figure 5a,b, Raman spectroscopy and electron paramagnetic resonance analyses reveal abundant defect structures in the BCN catalyst. The homogeneous elemental

distribution and abundant defect structures in BCN promote the formation of Lewis acid sites (undercoordinated B sites) and Lewis base sites (undercoordinated N sites), both of which accelerate N_2 activation. Benefiting from these structural advantages of BCN, the catalyst exhibited a high Faradaic efficiency of 27.2% at -0.29 V vs. RHE and an ammonia yield of $5.21 \mu\text{g h}^{-1} \text{mg}_{\text{cat}}^{-1}$ at -0.49 V vs. RHE, along with excellent long-term durability, outperforming most previously reported catalysts. Yu [41] successfully developed a metal-free electrocatalyst (BG) by the thermal annealing of graphene oxide and boric acid, which significantly enhanced the NRR catalytic performance of BG compared with undoped graphene, with a NH_3 yield of $9.8 \mu\text{g h}^{-1} \text{cm}^{-2}$ in an aqueous solution under ambient conditions at -0.5 V vs. RHE at a doping level of 6.2% and a Faradaic efficiency of 10.8%. As shown in Figure 5f,g, density functional theory calculations reveal the catalytic activity of different boron-doped carbon structures, among which the BC_3 structure has the lowest energy barrier for the electroreduction of N_2 to NH_3 .

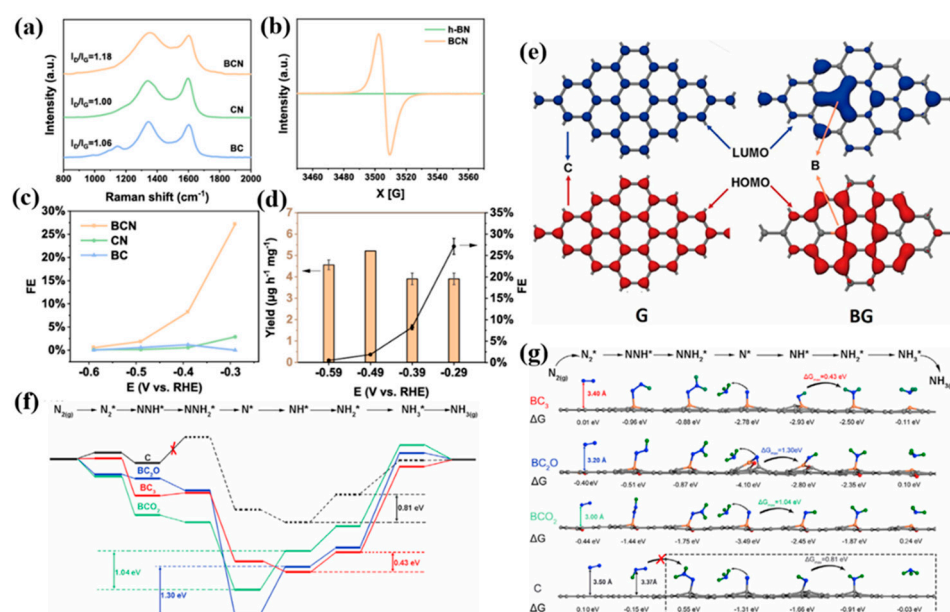


Figure 5. (a) Raman spectra of BCN, CN, and BC [40]; (b) EPR signals of BCN and h-BN [40]; (c) NH_3 Faradaic efficiency of BCN, CN, and BC [40]; (d) FE and ammonia yields of BCN at different potentials [40]; (e) LUMO (blue) and HOMO (red) of undoped G (left) and BG (right) [41]; (f) NRR free energy step plots on BC_3 , BC_2O , BCO_2 , and C [41]; (g) NRR reaction pathways and corresponding energy changes for BC_3 , BC_2O , BCO_2 , and C, with dotted rectangular boxes indicating steps that cannot be performed [41].

Sakshi et al. [42] successfully synthesized and characterized defective carbon catalysts (FBDGs) doped with triheteroatoms (N, B, and F) using a stepwise synthesis method, and the unique interaction between boron, nitrogen, and fluorine dopants promoted the formation of active centers with empty orbitals, enabling σ and anti π interactions with N_2 molecules. Theoretical studies indicate that FBDG exhibits a low overpotential, which enhances its applicability and increases the absorption energy of N_2 through the co-doped defective structure, which is conducive to breaking the strong triple bond in the N_2 molecule, thereby increasing the NRR; the Faradaic efficiency of the FBDG catalyst is 38.1%.

The advantages of non-metallic catalysts include environmental compatibility, low cost, and facile functionalization; however, they also face challenges, such as insufficient activity and unclear mechanism. Regarding catalytic activity, non-metallic catalysts generally exhibit lower turnover frequencies compared to metal catalysts, resulting in slower reaction kinetics and often necessitating elevated temperatures or pressures to achieve desirable conversion rates. In terms of stability, some non-metallic catalysts are susceptible to the re-

action environment, such as changes in temperature, pressure, atmosphere, etc., which may lead to changes in their structure and performance, thereby losing their catalytic activity. Regarding selectivity, non-metallic catalysts often display a limited ability to guide reaction pathways, which can result in undesired side reactions and diminished yields of target products in multi-component systems. Current research can focus on heteroatom doping, single-atom site manipulation, and the development of biomass-derived catalysts [43] to further improve their performance. As green chemistry advances, non-metallic catalysts are expected to play increasingly significant roles in clean energy production, pollution abatement, and sustainable chemical manufacturing.

The catalytic performances of the electrocatalysts reported to date are detailed in Table 1. In the process of the NRR system, most studies categorize mechanistic pathways as either dissociative or associative [38]. Precious metals, owing to their electronic configurations and pronounced chemisorption properties, preferentially facilitate the dissociative pathway. However, their continuous d-band electron layer will lead to the acceleration of the HER competition reaction, which is not conducive to the precipitation of products. In contrast, non-precious metals and non-metallic catalysts predominantly operate via the associative pathway due to structural diversity, creating multiple, tunable balances between activity and selectivity. Nonetheless, the intrinsic conductivity of metallic elements also promotes competing HER, constraining the catalytic efficiency. Non-metallic catalysts possess broad selectivity characteristics, but significant improvements in the turnover frequency and Faradaic efficiency are still needed, which may be achieved through heteroatom doping strategies.

Table 1. Representative catalysts and their key catalytic parameters.

Catalyst	Electrolyte	Reference Electrode	Potential (V vs. RHE)	Ammonia Yield	Faradaic Efficiency (%)	Ref.
Pt SAs/WO ₃	0.1 M K ₂ SO ₄	-	-0.2	342.4 µg h ⁻¹ mg ⁻¹	31.1	[25]
Ru@ZrO ₂ /NC	0.1 M HCl	Ag/AgCl	-0.21	3665 µg·h ⁻¹ ·mg ⁻¹	21	[26]
FeMoS ₂ /CC	1.0 M KOH	Hg/HgO	-0.3	2.74 µg h ⁻¹ mg ⁻¹	0.15	[32]
Cu ₃ Ag NSs	0.1 M Na ₂ SO ₄	Ag/AgCl	-0.2	31.3 µg h ⁻¹ mg ⁻¹	31.3	[34]
BCN 1.0B	0.1 M KOH	-	-0.49	5.21 µg h ⁻¹ mg ⁻¹	27.9	[40]
BG-1	0.05 M H ₂ SO ₄	Ag/AgCl	-0.5	55.1 µg h ⁻¹ mg ⁻¹	(-0.29 V vs. RHE) 10.8	[41]
FBDG	0.1 M Na ₂ SO ₄	-	-0.5	12.3 µg h ⁻¹ mg ⁻¹	38.1	[42]
B/O-CNNTs	0.05 M H ₂ SO ₄ +0.1 M Na ₂ SO ₄	-	-1.1	16.7 µg h ⁻¹ mg ⁻¹	35	[43]

Electrocatalytic nitrogen reduction (NRR) research requires rigorous experimental protocols due to the low yields of target products and the significant risk of background contamination. To ensure credible conclusions, this review highlights the necessity of multi-level, cross-validated control experiments. These controls can be grouped into three main categories. First, the nitrogen source must be established, typically by using high-purity ¹⁵N₂ gas for isotope labeling and detecting the ¹⁵NH₄⁺ signal via NMR or mass spectrometry [25,26,40,42,43]. Essential control experiments, including the Ar atmosphere blank test, open-circuit potential test, and catalyst-free control, systematically exclude false positives [25,32,34,40]. Second, the cross-quantification of products and by-product screening should be performed. At least two independent methods, such as the indigo blue method, sodium phenol sodium hypochlorite method, Knott's reagent method, or ion chromatography, are recommended for ammonia quantification [26,34,41,42]. The by-product hydrazine (N₂H₄) can also be detected to accurately calculate the Faradaic efficiency, using the Watt and Chrisp method [25,26,32,34,42,43]. Third, the strict pretreatment and purification of electrolytes, gases, and experimental equipment are essential, such as purifying the reaction inlet gas with effective purification devices, such as acid-base traps [42]. This review adopts these criteria to critically evaluate and present the literature data, with the

goal of establishing a framework for best practices and promoting reliable development in the field.

3. In-Depth Discussion of the NRR

3.1. Reaction Mechanisms of the NRR

The nitrogen reduction reaction (NRR) on catalysts typically proceeds through three main steps. First, N_2 molecules are chemically adsorbed onto the catalyst surface. Next, the adsorbed N_2 molecules undergo hydrogenation to form two NH_3 molecules. Finally, the resulting NH_3 molecules desorb from the catalyst surface. As illustrated in Figure 6, based on the sequence of $N\equiv N$ bond cleavage and hydrogenation, the NRR mechanism is generally classified into two categories: the dissociative pathway and the associative pathway.

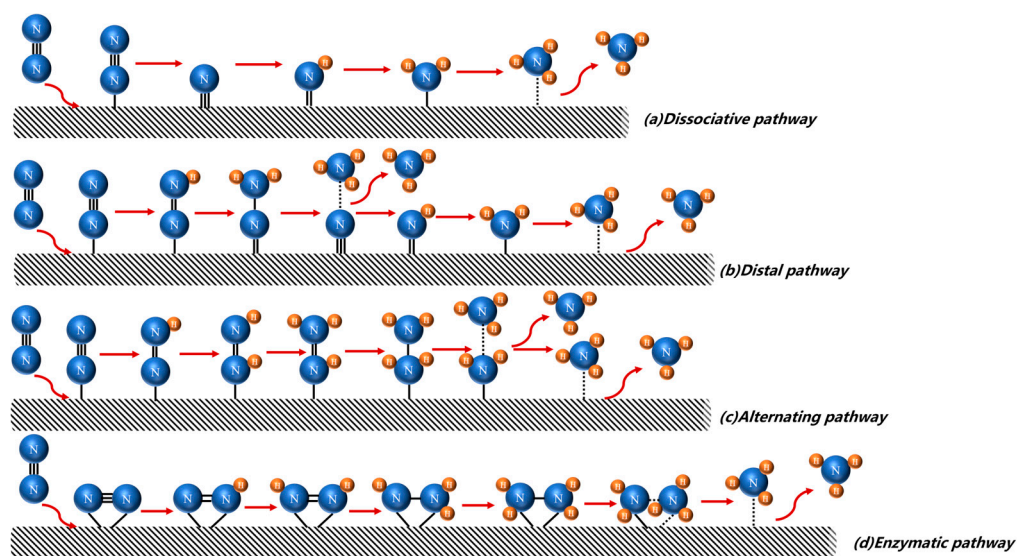


Figure 6. (a–d) Schematic depiction of the dissociative pathway and the associative pathway (including distal, alternating, and enzymatic pathways. The shaded part represents the catalyst surface) for the catalytic conversion of N_2 to NH_3 [44].

In the dissociation mechanism, the N_2 molecule is initially chemisorbed onto the catalyst surface. The $N\equiv N$ bond is then cleaved, producing two adsorbed nitrogen atoms ($*N$). These $*N$ atoms sequentially undergo proton–electron coupling, forming intermediates, such as $*NH$ and $*NH_2$ ($*$ The symbol is used to indicate the intermediates adsorbed on the surface of the catalyst), which ultimately yield NH_3 that desorbs from the surface. Overcoming the high dissociation energy barrier of the $N\equiv N$ bond typically requires an elevated temperature and pressure, as exemplified by the Haber–Bosch process. Certain transition metals, including molybdenum and tungsten, can partially facilitate $N\equiv N$ bond dissociation at room temperature due to their strong interactions with nitrogen atoms, which aligns with the dissociation mechanism. In contrast, the association mechanism activates nitrogen molecules through stepwise hydrogenation without complete bond cleavage. In this process, N_2 is adsorbed onto the catalyst surface and subsequently reacts with proton–electron pairs to generate hydrogenated nitrogen intermediates. Based on the hydrogenation site, the association mechanism is classified into distal, alternating, and enzymatic pathways. Most transition metal-based electrocatalysts, such as iron, cobalt, and nickel, predominantly follow the association mechanism at room temperature. The moderate adsorption energy of N_2 on these catalyst surfaces is sufficient to activate the $N\equiv N$ bond while avoiding excessive stabilization of hydrogenation intermediates, thereby maintaining reaction reversibility and facilitating product release.

3.2. Methodologies for Reliable NH_3 Detection

The primary means of assessing the effectiveness of the NRR is the precise detection and quantitative analysis of NH_3 . The indophenol blue method [25,26,32,34,40–42] and nuclear magnetic resonance (^1H NMR) method are currently the most widely used detection techniques. Every technique has certain situations and places of operation that must be chosen sensibly based on the experimental setup.

The color reaction of NH_3 with sodium hypochlorite and salicylic acid in an alkaline environment to produce a blue indophenol complex is the basis for the indophenol blue colorimetric method. The concentration of NH_3 has a linear relationship with the absorbance at 650 nm. Although the procedure is straightforward and inexpensive, the reaction conditions must be closely monitored. The chemical shift difference between $^{14}\text{NH}_4^+$ and $^{15}\text{NH}_4^+$ in the NMR spectrum allows the ^1H NMR approach to perform both qualitative and quantitative analyses of NH_3 . The main benefit of this approach is that the $^{15}\text{N}_2$ isotope tagging experiment effectively distinguishes the source of the product NH_3 . The ^1H NMR approach is frequently combined with the indophenol blue method [32,34,42].

4. Conclusions

In the realm of green chemistry, the research on electrocatalysts for N_2 reduction to NH_3 under environmental conditions has grown in importance. Researchers are looking for alternatives in mild climates due to the standard Haber–Bosch process's excessive energy usage and environmental impact. Due to its sustainability and environmental friendliness, electrocatalysis has advanced significantly in recent years. This method can be used in conjunction with new, intermittent, and volatile energy sources, like solar, wind, and tidal energy, to address the storage issue. The main obstacle to using this technology is the absence of a high-efficiency electrocatalyst that is appropriate for large-scale industrial production and consistent with the initial goal of conserving green energy.

We provide an overview of the most recent advancements in room-temperature NRR electrocatalysts in this paper. In order to overcome the fundamental bottleneck of “activity–selectivity–stability”, the creation of high-efficiency catalysts depends on the cooperative investigation of non-precious metals, precious metals, and non-metal catalysts. Many studies in the past concentrated on optimizing a single performance, but the present research indicates that the exact control of the electronic environment and the spatial arrangement of the active sites is the universal approach for all three types of catalysts. Through electronic coupling, non-precious metals can create diatomic synergistic sites to maximize the d-band center. Precious metals must investigate alloying techniques and fortify the strong contact between single atoms and carriers. Non-metals can develop heteroatom gradient doping and porous structures to improve mass transfer efficiency. Mechanism research needs to combine in situ characterization techniques to track the valence changes in active sites and the evolution of intermediates, and use machine learning to construct a “structure–activity” model to accelerate screening. The performance of non-precious metal catalysts is better than that of precious metal catalysts and metal-free catalysts in large-scale production. Furthermore, its abundant supply of materials and affordability indicate the path for further investigation and use of electrocatalyst materials. In addition, precious metals dominate high-precision micro-synthesis, and non-metals expand green scenarios. The three catalysts complement each other in different scenarios.

However, there are still many challenges in this field, such as the chemical inertness of N_2 molecules, the interference of HER competing reactions, and the contradiction between catalyst stability and large-scale application. Future research should focus on multi-scale collaborative optimization strategies and promote the industrial application

of N₂ electroreduction to NH₃ under environmental conditions through material design optimization, reaction mechanism analysis, and process innovation.

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Abbreviations

The following abbreviations are used in this manuscript:

NRR	Electrocatalytic nitrogen reduction reaction
HER	Hydrogen evolution reaction
CO ₂ RR	CO ₂ reduction reaction
ORR	Oxygen reduction reaction
NORR	Electrocatalytic NO reduction reaction
HF	Hydrofluoric acid
FE	Faradaic efficiency
DFT	Density functional theory

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