

Recent advances in robust ammonia synthesis from nitrate reduction through MXene-based electrocatalysts: from fundamental and development to machine-learning

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ABSTRACT: Ammonia (NH₃) is a key chemical feedstock, a carbon-free fuel, and a hydrogen carrier, yet its production still relies on the energy- and emission-intensive Haber-Bosch process. Electrocatalytic nitrate reduction (eNO₃⁻RR) offers a sustainable alternative, converting NO₃⁻ and water to NH₃ under ambient conditions, but it demands catalysts that combine high activity, selectivity, and stability. Two-dimensional transition-metal carbides, nitrides, and carbonitrides (MXenes) are promising candidates because of their high electrical conductivity, large surface area, and tunable surface chemistry, although their use in eNO₃⁻RR remains underexplored. This review covers the mechanisms of nitrate-to-ammonia conversion and the synthesis of MXenes, then analyzes how noble-metal decoration, alloying, hybridization with metal compounds, and single-atom engineering shape catalytic performance. It also examines how machine-learning-assisted computational modeling can predict and optimize MXene-based catalysts. Finally, key challenges and future directions are outlined to guide the rational design of MXene electrocatalysts for green ammonia synthesis.

KEYWORDS: Ammonia, Electrocatalytic, Renewable energy, Nitrogen reduction, Hydrogen carrier, Machine Learning.

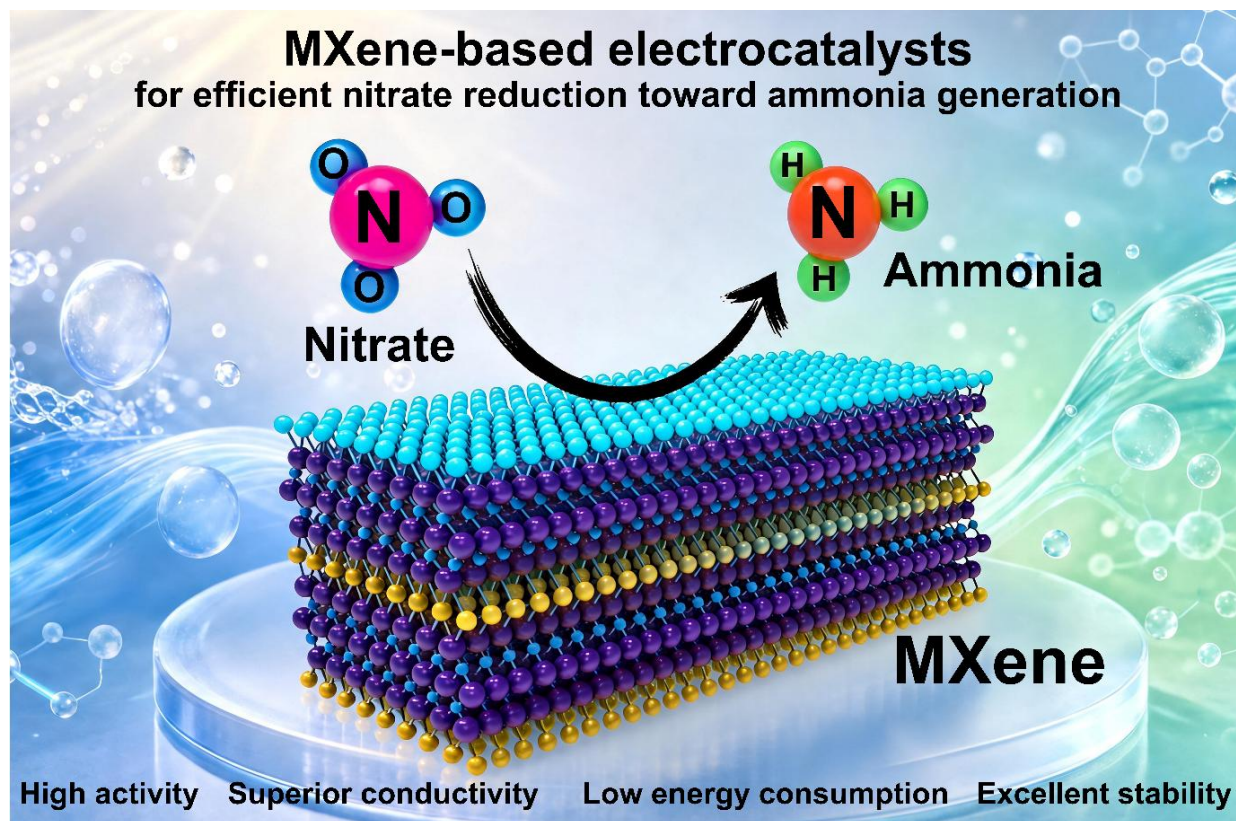
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Graphical abstract



1. Introduction

The rapid expansion of industrialization and continued population growth have placed growing pressure on global energy systems. As a result, energy consumption has risen to levels that are becoming increasingly difficult to sustain. This surge in demand, combined with our heavy and longstanding dependence on conventional energy sources, has triggered a range of serious environmental consequences, one of the most pressing challenges of our time.^[1] According to the Energy Institute's Statistical Review of World Energy 2023, fossil fuels, including coal, petroleum, and natural gas, continue to account for roughly 82% of the world's primary energy supply. Although these resources are economically essential, their large-scale extraction and combustion release a variety of harmful byproducts.^[2] The combustion of carbon-based fuels releases significant quantities of greenhouse gases and air pollutants, including carbon dioxide (CO₂), carbon monoxide (CO), sulfur dioxide (SO₂), nitrogen oxides (NO_x), and various volatile organic compounds such as methane, benzene, formaldehyde, and ethanol. Among these emissions, CO₂ plays the dominant role in driving

anthropogenic climate change, with industrial fossil fuel combustion accounting for approximately 80% of total atmospheric CO₂ inputs.^[3] These emissions contribute to air pollution, ecological damage, and the ongoing alteration of global climate patterns.^[2]

As the urgency of decarbonization grows, governments worldwide are translating ambitious emissions-reduction goals into formal national policies. Particularly, China has pledged to peak its carbon emissions by 2030 and achieve carbon neutrality by 2060. This represents a significant reorientation in how major emitting economies are aligning their long-term development strategies with climate objectives.^[4]

Over the past few decades, efforts toward sustainable, clean energy sources have accelerated considerably, fueled by growing environmental concerns and the pressing need to reduce reliance on carbon-intensive fossil fuels. Developed technologies such as solar, wind, hydroelectric, geothermal, and bioenergy have drawn substantial research attention and commercial investment as key pathways to achieve a low-carbon energy system. However, the intermittent nature of many of these renewable resources, together with their uneven geographic availability, continues to

pose significant challenges to a smooth and complete transition away from conventional fossil fuel-based energy systems.^[5]

In this context, hydrogen (H_2) emerges as a particularly promising energy carrier. Unlike coal or petroleum-derived fuels, its combustion produces only water, generating no toxic byproducts or greenhouse gases. This inherent cleanliness eliminates the need for expensive downstream waste-treatment infrastructure.^[6] In recent years, hydrogen technologies have advanced significantly and now compete effectively with established low-carbon alternatives, in both technical performance and cost. A clear demonstration of this competitiveness can be seen in recent economic modeling of large-scale power generation. Analyses of a 500 MW combined-cycle plant show that retrofitting a fossil fuel system with carbon capture infrastructure increases costs by approximately 30% compared with an equivalent hydrogen-fueled plant.^[7] However, the widespread practical use of H_2 as an energy carrier is still hindered by significant challenges in storage and transportation. Hydrogen possesses an exceptionally high gravimetric energy density of 119.7 MJ kg^{-1} , yet its volumetric energy density, even in liquid form, is relatively modest at 8.96 GJ m^{-3} . Adding to these difficulties, H_2 molecules readily diffuse into many structural materials, causing embrittlement that gradually weakens and degrades the containment systems over time.^[8]

Cryogenic liquid hydrogen offers a significantly higher volumetric energy density of approximately 70 kg m^{-3} when stored at -253°C . However, the liquefaction process itself is highly energy-intensive, consuming roughly 30% of the hydrogen's heating value. In addition, the fuel must be kept in heavily insulated, specially designed storage vessels to minimize boil-off losses, which substantially increases the overall cost of the system.^[9]

One effective way to overcome the technical challenges of storing and transporting hydrogen is to bind it chemically to stable carrier molecules. Ammonia, methanol, and methane have emerged as leading candidates, each offering distinct trade-offs in handling ease and energy density. Among them, ammonia occupies a uniquely attractive position: it is the only carbon-free chemical energy carrier currently considered viable for large-scale deployment in the transportation sector, making it a focal point of growing research and policy interest.^[5]

Ammonia (NH_3) is a critical global commodity for fertilizer, pharmaceutical, and chemical manufacturing, and also serves as a promising carbon-free energy carrier due to its high hydrogen content (17.5 wt% H_2).

In 2020, worldwide NH_3 production reached approximately 182 million metric tons, almost entirely through the Haber-Bosch (H-B) process, often regarded as the most influential invention of the 20th century.^[10] In addition, ammonia benefits from well-established production and transportation infrastructure, including existing pipelines and global shipping networks. It was reported that around 150 Mt of NH_3 is produced and distributed annually via marine, road, rail, and pipeline systems. At the point of use, H_2 can be readily obtained through ammonia decomposition.^[11] Nevertheless, the H-B process is highly energy-intensive, requiring harsh conditions (typically $350\text{--}450^\circ\text{C}$ and 100–200 bar) to overcome the strong $N\equiv N$ triple bond. This accounts for about 1% of global annual energy consumption and contributes over 1.4% of worldwide CO_2 emissions. Furthermore, 77% of the hydrogen used in ammonia synthesis comes from steam reforming of natural gas, with each ton of NH_3 generated, releasing roughly 2.1 tons of CO_2 .^[10] Therefore, there is an urgent need to develop more sustainable ammonia synthesis routes that operate under milder conditions ($< 400^\circ\text{C}$ and < 200 bar) with improved efficiency to lower the carbon footprint and help address climate change.^[12]

Recently, the “green ammonia” approach has emerged as a promising alternative to the traditional H-B process, owing to its mild operating conditions and compatibility with renewable energy sources. Among the various approaches, the electrochemical reduction of nitrogen (N_2) (eNRR) has attracted considerable attention and has shown notable advancements.^[13] Its practical implementation, however, is limited by several intrinsic obstacles, such as the substantial energy required to cleave the highly stable $N\equiv N$ triple bond, weak interaction between non-polar N_2 molecules and the catalyst's active sites, and the very low solubility of N_2 in aqueous electrolytes.^[14, 15] Notably, nitrate (NO_3^-) offers unique advantages as nitrogen sources for the electro-synthesis of NH_3 because the bond energy of polar $N=O$ bond (204 kJ mol^{-1}) is four times lower than that of the non-polar $N\equiv N$ bond (941 kJ mol^{-1}), allowing the $N-O$ bond to be readily activated at lower energies.^[15, 16] Moreover, nitrate ions are among the most widespread water pollutants worldwide, released into terrestrial and aquatic environments primarily through human activities, liquid nuclear wastes, livestock manure, and chemical fertilizers, resulting in significant environmental pollution.^[17, 18] It was reported that at concentrations exceeding 10 mg L^{-1} , nitrate can cause serious health problems, including methemoglobinemia, and contributes to the formation of carcinogenic N-nitroso compounds.^[19] Thus,

removing excess nitrate from contaminated water is essential to close the artificial nitrogen cycle.

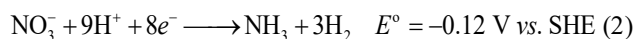
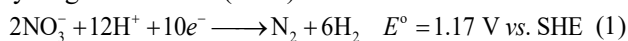
To date, extensive efforts have been made to develop selective catalysts for the eNO_3^- -RR in alkaline and neutral media. Although state-of-the-art catalysts have achieved high Faradaic efficiencies (FE) for NH_3 (> 90%) and substantial overpotentials remain required to achieve optimal NO_3^- -to- NH_3 performance.^[20] In this process, several intermediate substances (like NO_2^- , NO , N_2O , etc.) can form. The formation of these intermediates reduces ammonia production and may also cause catalyst deactivation or poisoning, further diminishing reaction efficiency. In addition, during extended reaction times, the catalyst may undergo structural changes, including aggregation, dissolution, or phase transitions, which can reduce its effectiveness and stability.^[21] For instance, transition metal-based electrocatalysts (e.g., copper (Cu), cobalt (Co), and nickel (Ni)) have shown considerable promise for eNO_3^- -RR. Besides, the *d*-orbital electrons in these metals readily promote metal-H bond formation, which intensifies the competing hydrogen evolution reaction (HER) and thereby limits eNO_3^- -RR efficiency.^[22] Noble metal-based electrodes, such as those containing Pd and Ru, have been investigated as electrocatalysts for this reaction; however, their high cost and scarcity restrict large-scale deployment.^[23]

A novel family of two-dimensional (2D) transition metal carbides/nitrides called MXenes has recently garnered increasing interest in electrocatalysis and photoelectrocatalysis because of their ultrathin structure, superb conductivity, and abundant chemical variety.^[22, 24–28] Over the past five years, extensive research has explored the layered MXene potentials to enhance various electrocatalytic reactions.^[29–44]

However, dedicated reviews that specifically address the rational design of electrocatalysts for the selective reduction of NO_3^- to NH_3 remain scarce. Therefore, this review summarizes recent progress in catalysts for the eNO_3^- -RR aimed at achieving high ammonia yields, Faradaic efficiencies, and selectivity under ambient conditions. Before discussing the synthesis procedure of MXene-based electrocatalysts, the fundamental principles and mechanistic pathways governing the NO_3^- reduction reaction are first outlined in the following section to provide the necessary theoretical framework for understanding catalytic performance. Next, the latest developments in electrocatalysts, including noble metals, single-atom catalysts, and transition-metal-based materials and compounds, are presented. Finally, the current challenges and future perspectives in this field are outlined.

2. Mechanism of NH_3 synthesis by eNO_3^- -RR

The electrochemical reduction of nitrate includes reactant diffusion, adsorption, charge transfer, product desorption, and separation, potentially generating various nitrogen-containing compounds, with nitrogen and ammonia being the most thermodynamically stable products.^[45] In general, nitrate reduction is a complex multi-electron transfer process that involves a range of nitrogen-containing intermediates with oxidation states spanning from +5 to –3.^[46] In this process, N_2 and ammonia/ammonium ($\text{NH}_3/\text{NH}_4^+$; $\text{pK}_a = 9.25$), the most thermodynamically stable end products, have been the subject of extensive research. From an environmental protection viewpoint, the production of harmless N_2 gas is the most desirable outcome; however, with the goal of “turning waste into wealth,” recyclable NH_3 is the preferred target product. The key related reactions are shown in **Eqs. (1) and (2)**, where the electrode potentials (E°) are given relative to the standard hydrogen electrode (SHE).^[47]



From this perspective, electrochemical conversion of NO_3^- to NH_3 generally proceeds via two electrocatalytic pathways: direct and indirect mechanisms, depending on the concentration and pH of electrolytes. The direct mechanism can take place at any nitrate concentration and features two determining steps (rate-determining and selectivity-determining) along with a key intermediate (NO_{ads} , see below). Moreover, the indirect mechanism occurs only in the presence of nitrite (> 10^{-6} M) and at high NO_3^- concentrations (1.0–4.0 M).^[48]

2.1. Direct electrocatalytic reduction mechanism

In the direct reduction mechanism, nitrate is the electroactive species and participates directly in electron transfer. As shown in **Fig. 1a**, this process operates via two distinct mechanisms: one governed by active adsorbed hydrogen (H_{ads}) and the other by cathodic electron transfer.^[47] This process typically consists of three essential stages: the adsorption of NO_3^- ; the reduction of NO_3^- to NO_2^- (commonly the rate-limiting step); and the reduction of NO_2^- to NH_3 or N_2 (the step that determines selectivity).^[49]

Under neutral and alkaline conditions, NO_3^- reduction is mediated by H_{ads} ^[50], and in this pathway, the initial step is the generation of H_{ads} via the

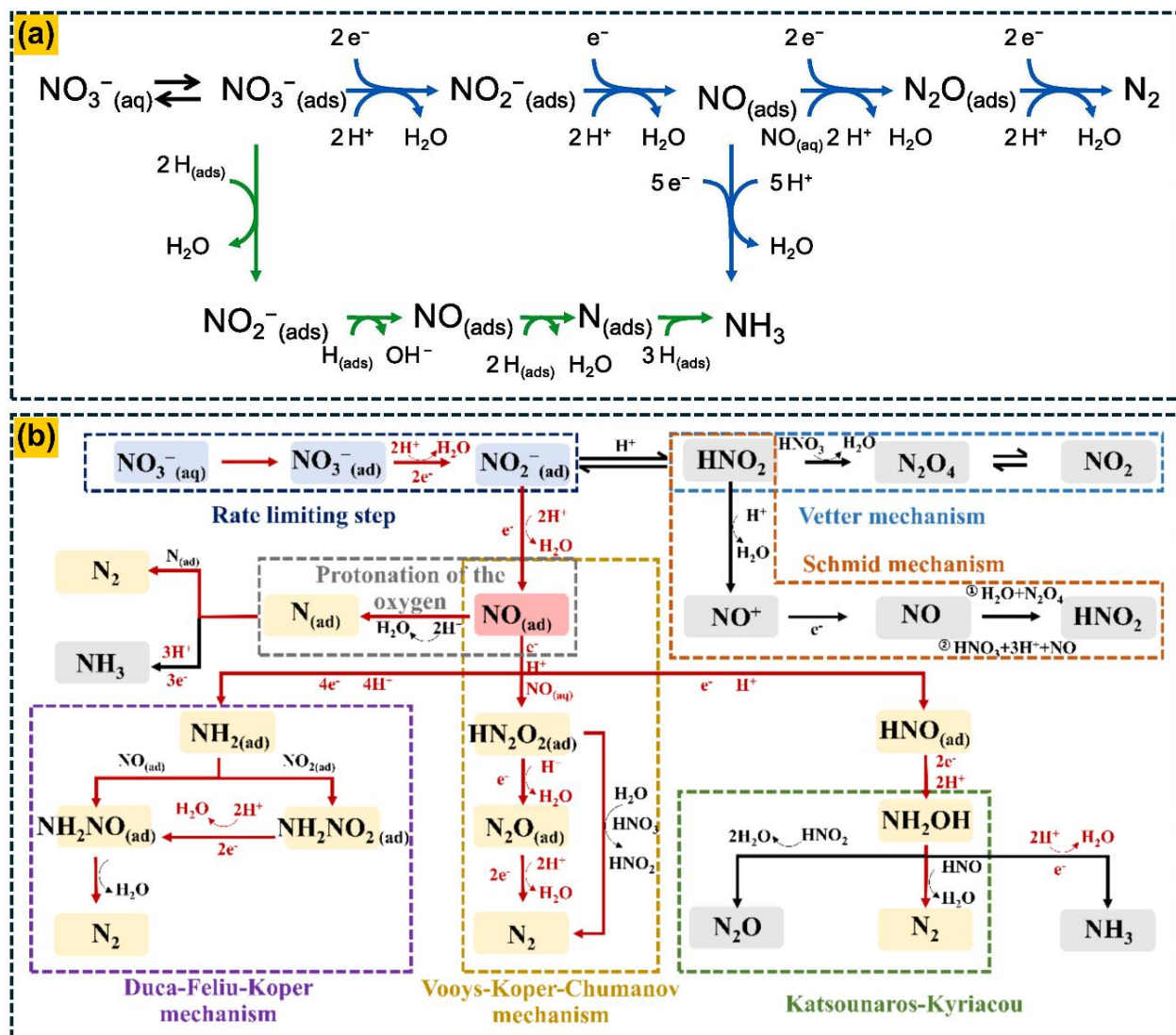
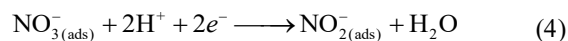
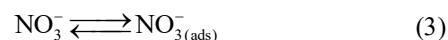
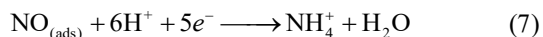
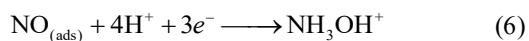
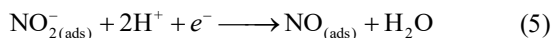


Figure 1. (a) The direct mechanism for electrochemical nitrate reduction mediated by electron transfer (blue arrow) and atomic hydrogen (green arrow).^[54] (Copyright 2021, Elsevier) (b) A map of the mechanisms and main processes involved in the electrochemical reduction of nitrate.^[55] (Copyright 2025, Elsevier)

decomposition (dissociation) of adsorbed water on the cathode surface. In addition, in the electron-mediated pathway, electrons directly reduce adsorbed NO_3^- on the cathode surface to nitrite. Typically, the conversion of NO_3^- to NO_2^- requires a high activation energy and is the rate-determining step governing the overall kinetics of the nitrate reduction reaction. The resulting adsorbed NO_2^- is subsequently reduced to adsorbed nitric oxide ($\text{NO}_{(\text{ads})}$), as a critical branching intermediate, that determines whether the reaction proceeds toward N_2 or $\text{NH}_3/\text{NH}_4^+$.^[13] Mediated by the atom H_{ads} , the creation of N-H bonds is more active compared to the formation of N-N bonds, leading to

ammonia being the primary product. Importantly, this process of is typically conducted at a low overpotential, crucial for minimizing side reactions.^[50] It is worth to mention that the electrochemical reduction of atomic H_{ads} is especially significant for catalysts based on precious metals, like Pd-based materials, which exhibit a high affinity for hydrogen.^[49] By integrating the findings from previous reported results and mechanisms, Dima *et al.*^[51] proposed the following mechanism:



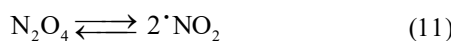
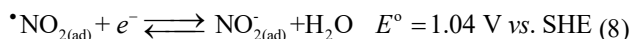


Another typical route involves a sequence of direct charge transfer reactions in succession. In this process, initially, the NO_3^- in the solution adheres to the catalyst's surface to create $^*\text{NO}_3^-$, after which N-O is cleaved to generate $^*\text{NO}_2^-$. Since the lowest unoccupied orbital of NO_3^- possesses higher energy, it loses an electron to $^*\text{NO}_2^-$. The generation of $^*\text{NO}_2^-$ is the rate-limiting step of $\text{eNO}_3^- \text{RR}$.^[50]

2.2. Indirect electrocatalytic reduction mechanism

The indirect electrocatalytic reduction of nitrate is also referred to as the autocatalytic reaction mechanism.^[52] In this procedure, nitrate itself is not directly reduced at the electrode surface; instead, it is first converted to an intermediate species, which then participates in the electron transfer step.^[13] This pathway takes place in acidic pH conditions and at elevated reactant concentrations (usually 1.0-4.0 M), with the reduction occurring via key intermediates like NO^+ and NO_2 that trigger autocatalytic reactions instead of through direct electron transfer to NO_3^- .^[49] These autocatalytic processes can mainly be classified into the Vetter and Schmid mechanisms, as depicted in Fig. 1b.

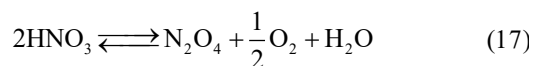
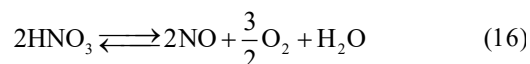
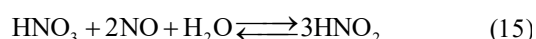
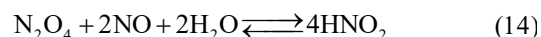
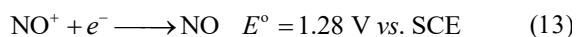
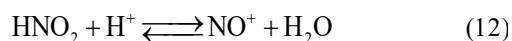
In the Vetter mechanism, a key intermediate (often denoted as $^*\text{NO}_2$) serves as the electroactive substance. Firstly, NO_2^- can be generated according to Eq. (8). Under strongly acidic conditions, this reaction leads to the formation of nitrous acid (HNO_2) via Eq. (9). The cycle is then completed by the regeneration of other intermediates through Eqs. (10) and (11). From Eqs. (8)-(11), it is evident that each molecule of the autocatalytic intermediate entering the cycle ultimately produces two molecules of the same intermediate, enabling the self-sustaining (autocatalytic) nature of the reaction.^[48, 53]



On the other hand, in the Schmid mechanism, the key electroactive species is the nitroso ion (NO^+), produced by protonation of nitrite under highly acidic conditions (Eq. (12)). As can be seen in Eq. (13), NO^+

can be reduced to NO ($E^0 = 1.28 \text{ V vs. SCE}$), and the product is then formed through the interaction of NO with NO^+ (Eq. (14)). That said, some researchers consider the pathway in Eq. (15) to be preferred over Eq. (14). When the nitrate concentration exceeds 4.0 M, alternative reactions (Eqs. (16) and (17)) replace the original reactions. These equilibria then shift to the right, producing N_2O_4 and NO . Although both NO and N_2O_4 can ultimately form HNO_2 , this conversion does not involve electrochemical charge transfer. Therefore, this step is not included in the autocatalytic reaction mechanism.^[48]

In summary, indirect reduction mechanism has been extensively discussed in initial reports, yet it shows limited controllability and often generates many by-products, rendering it unsuitable for selective ammonia synthesis. For example, NO_2 and HNO_2 generated by the Vetter and Schmid pathways can easily be further converted into N_2O or N_2 instead of the desired product NH_3 . Consequently, more research should concentrate on creating catalysts that achieve high selectivity in mildly acidic or neutral environments to avoid the issues linked to the indirect pathway.^[49]



3. MXene: Preparation and Properties

In 2011, a new family of 2D materials, transition metal carbides, nitrides, or carbonitrides (MXenes), was introduced by Drexel scientists and has since become prominent in catalysis.^[56, 57] MXenes are commonly prepared by selective etching of $\text{M}_{n+1}\text{AX}_n$ ($n = 1-3$) precursors to yield $\text{M}_{n+1}\text{X}_n\text{T}_x$ (Fig. 2a), where M is an early transition metal (e.g., Ti, Nb, Ta, Mo), A is a group 13 or 14 element (e.g., Al, Si, Ga), X is C and/or N, and T_x represents surface groups.^[58] In the case of $\text{M}_{n+1}\text{X}_n\text{T}_x$, because surface terminations depend on the etching environment, their stoichiometric ratio is expressed as T_x , with x typically close to 2.^[59] Since

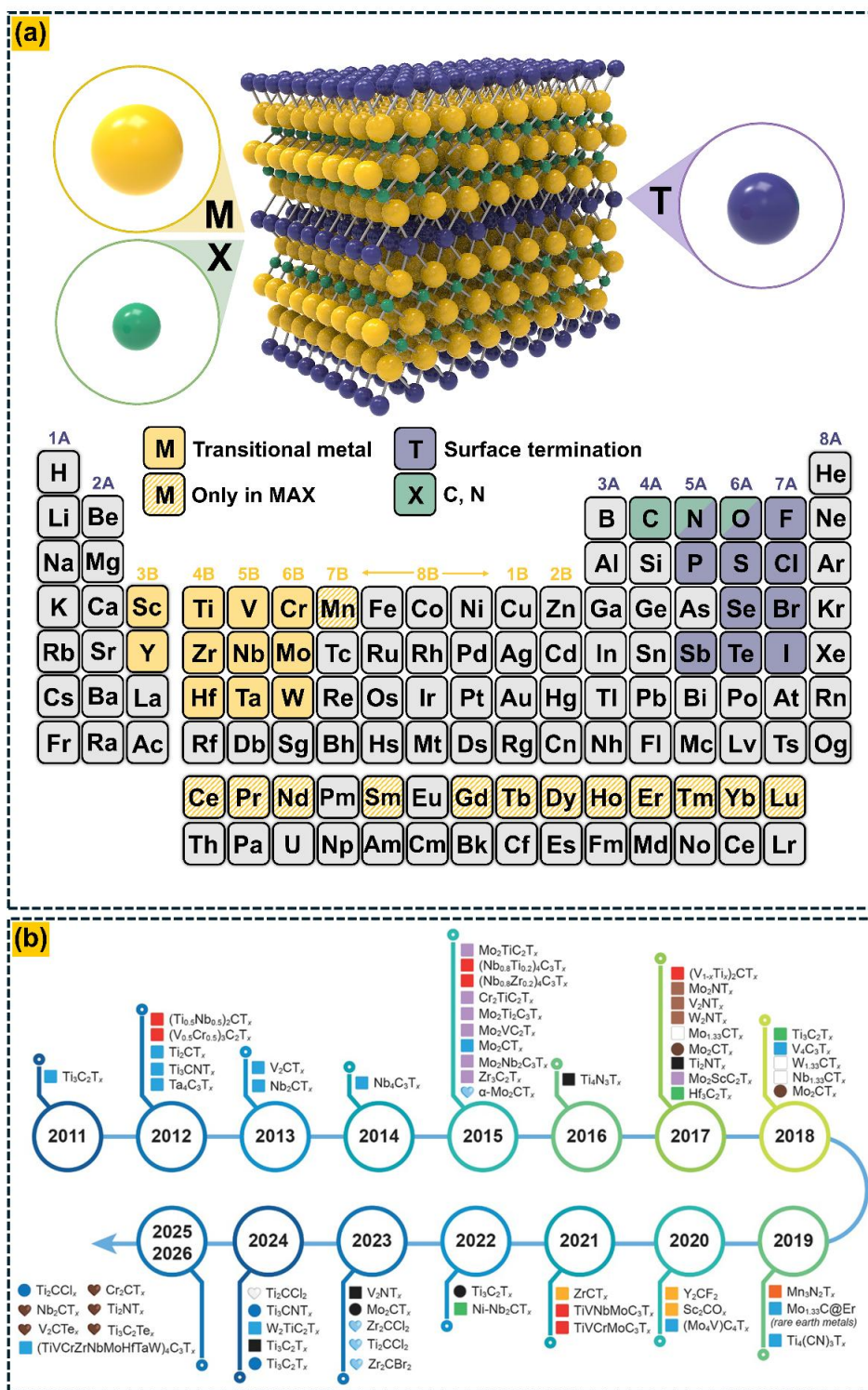


Figure 2. (a) The periodic table highlights the constituent elements of MXenes: metals (M elements) are marked with a yellow background, non-metals (X elements) with a green background, and terminating elements with a purple background. Rare-earth elements that can form in-plane ordered MAX structures are shown with a striped background, while elements reported exclusively in MXene precursors (MAX phases) are indicated with diagonal stripes. Oxygen is distinguished by diagonal stripes, reflecting its role in the recently discovered oxycarbide MXene. (b) Timeline of major milestones in the development of MXene from 2011 to 2026.^[60] (Copyright 2026, Wiley)

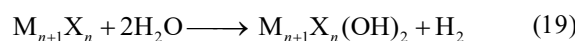
their discovery, the variety of experimentally confirmed MXene compositions has consistently increased (**Fig. 2b**)^[60], alongside swift advancements in eco-friendly and high-quality synthesis techniques for MXenes.^[31, 35, 37, 39, 41, 42, 61–68] Till now, more than 60 members of the MXene family have been synthesized, combining metallic and ceramic properties.^[29]

Analysis of the SCOPUS database, however, validates this increasing recognition, showing that catalysis researchers have progressively focused on MXenes since the field's rise over the last decade. The data reveal a significant, almost exponential increase in publications regarding this topic over the years that followed (**Fig. 3a**).^[69] Furthermore, an extensive study provides a broader view on MXenes in electrocatalysis, focusing on HER, due to its numerous connections to associated research fields, as shown in **Fig. 3b**. This illustration depicts the co-existing keywords linked to MXene-based hydrogen production through electrocatalysis, with connections sized by density and color to represent both experimental and computational viewpoints. The keyword network also emphasizes significant difficulties encountered by MXene electrocatalysts.^[70]

From this perspective, in electrocatalysis, $\text{Ti}_3\text{C}_2\text{T}_x$ remains the most widely studied MXene, consisting of three Ti layers and two C layers; however, achieving a uniform surface structure is challenging, and it often exhibits poor cycling stability. As another important member of the MXene family, Nb_2C has attracted considerable attention in recent years. Compared with $\text{Ti}_3\text{C}_2\text{T}_x$, Nb_2C possesses a thinner atomic structure, more exposed active sites, higher electrical conductivity, and a larger surface area.^[22] Subsequently, an increasing variety of MXenes, including Ti_2CT_x , TiNbCT_x , $\text{Ti}_3\text{CN}_x\text{T}_x$, $\text{Ta}_4\text{C}_3\text{T}_x$, Nb_2CT_x , V_2CT_x , $\text{Nb}_4\text{C}_3\text{T}_x$, Mo_2CT_x , $(\text{Nb}_{0.8}\text{Ti}_{0.2})_4\text{C}_3\text{T}_x$, $(\text{Nb}_{0.8}\text{Zr}_{0.2})_4\text{C}_3\text{T}_x$, $\text{Zr}_3\text{C}_2\text{T}_x$, and $\text{Hf}_3\text{C}_2\text{T}_x$, have been successfully developed.^[71]

Technically, the characteristics of the obtained MXenes depend heavily on the preparation method, since the formation of specific surface functional groups has a substantial impact on their performance.^[72] The synthesis procedure for MXenes generally involves chemical exfoliation of MAX phases via treatment with hydrofluoric acid (HF) or other etchants, such as lithium fluoride with hydrochloric acid ($\text{LiF} + \text{HCl}$) and ammonium bifluoride (NH_4HF_2).^[73] In this process, the Al atoms are replaced by O, OH, or F atoms, which weaken the interlayer interactions between the M_{n+1}X_n layers, allow their easy separation, and strongly influence the physicochemical properties of the resulting

materials.^[29, 73] As an example, 2D Ti_3C_2 was successfully prepared by exfoliation of Ti_3AlC_2 in 50% HF at room temperature for 2 h. The process proceeds according to the following reactions (**Eqs. 18–20**):^[74]



Importantly, water-based etching methods that use F-containing substances still pose significant toxicity and corrosion hazards, limiting the widespread manufacturing of MXenes. To address these issues, researchers have developed methods for synthesizing fluorine-free MXenes, such as electrochemical etching, ball milling, hydrothermal methods, chemical vapor deposition (CVD), and photo-Fenton techniques.^[75]

MXenes exhibit excellent electrical conductivity ($> 20000 \text{ S cm}^{-1}$ for $\text{Ti}_3\text{C}_2\text{T}_x$) and high volumetric capacitance as electrodes ($> 2800 \text{ F cm}^{-3}$ for $\text{Ti}_3\text{C}_2\text{T}_x$),^[76] along with a large specific surface area, rich surface chemistry enabled by facile functionalization, good dispersibility in solvents such as water, and excellent electrochemical properties that make it highly promising for catalytic applications.^[77, 78] Compared with other nanomaterials such as reduced graphene oxide and carbon nanotubes, MXenes deliver superior conductivity without requiring polymer binders or surfactants.^[76]

In particular, the outstanding intrinsic properties of MXenes give them strong potential for eNO_3^-/RR applications.^[79] In **Fig. 4**, the timeline illustrating the development of MXene-based catalysts toward eNO_3^-/RR from 2012 to 2023.^[79] However, intrinsic limitations, including low catalytic activity, susceptibility to oxidation, and severe nanosheet restacking, substantially impair their electrochemical performance by reducing the number of accessible active sites and restricting ion/electrolyte transport.^[21]

For instance, the surface functional groups of MXenes can create hydrogen-bond interactions with water molecules. The hydrophilicity of MXenes increases as the functional groups shift from -O and -F to -OH. As weak hydrogen-bond acceptors, -O and -F functional groups have limited access to water. In comparison, -OH functional groups act as hydrogen-bond donors, leading to shorter bonding distances and stronger interactions. It was observed that the electrocatalyst's suitable hydrophobicity might reduce H^+ adsorption and enhance NO_3^- diffusion at the electrode interface. While the hydrophobic inner surface can diminish H^+ reduction, some external

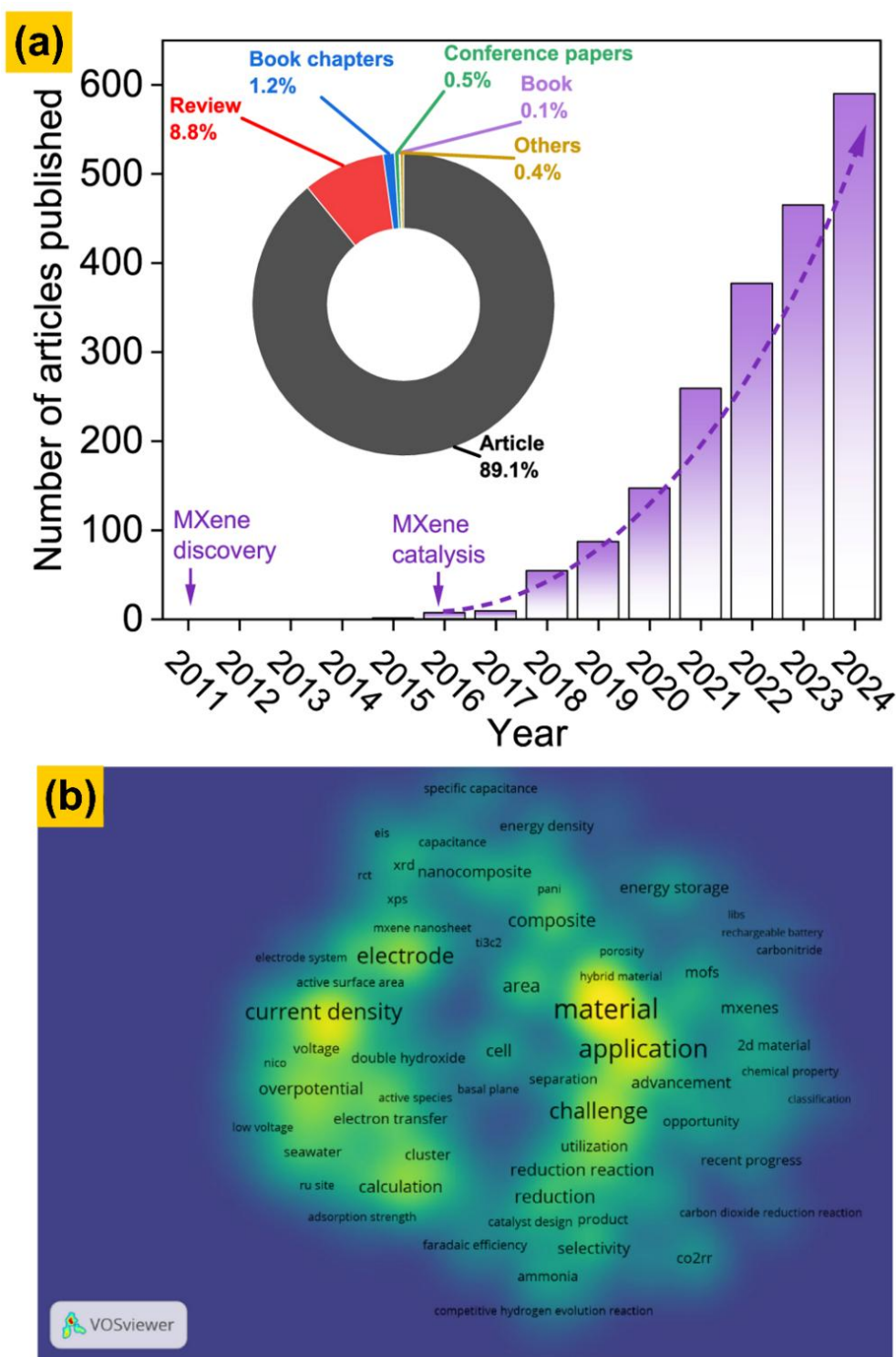


Figure 3. (a) Trend in MXene catalysis research indicating the cumulative number of publications on the topic since its inception. Inset shows the distribution of article categories for all published papers. Data were retrieved from the SCOPUS database utilizing the keywords ‘MXene’ and ‘Catalysts’ and searched in article titles, abstracts, and keywords.^[69] (Copyright 2025, IOPscience) (b) The framework diagram illustrating MXene as a material used in electrocatalysis for hydrogen generation and various research parameters was visualized with VOSviewer.^[70] (Copyright 2025, Elsevier)

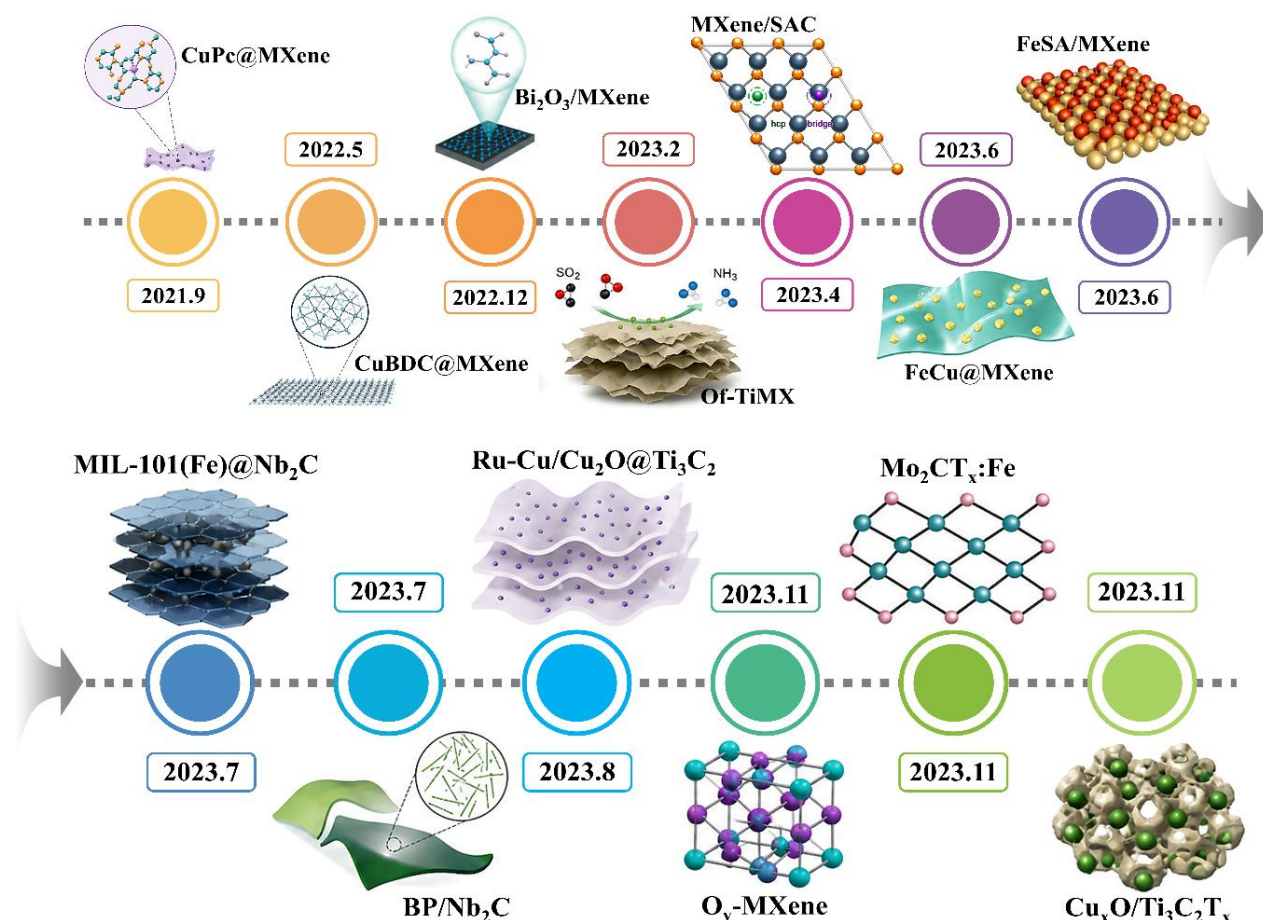


Figure 4. Summary of the MXene-based electrocatalysts for NO_3^- RR. The concept of this figure was inspired by Ref. [79].

hydrophilicity remains necessary for effective ion transport. Thus, MXene-based electrocatalysts with a hydrophobic interior and hydrophilic exterior are expected to optimize H^+ and NO_3^- adsorption efficiency, enhancing eNO_3^- RR kinetics.^[79]

Moreover, recent density functional theory (DFT) studies indicate that altering the surface functionality of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene could optimize eNO_3^- RR performance. Those MXenes with partial O vacancies appear favorable because they have a more negative d -band center and an elevated Ti oxidation state on the surface, which can reduce the $^*\text{NH}_x$ intermediate adsorption on their surface, thereby promoting hydrogenation. Besides, injecting charges from MXene into the lowest unoccupied molecular π^* orbital (LUMO π^*) of NO_3^- is not advantageous. This could trigger the infamous competing reaction, specifically the pathway to produce NO_2^- , linked to the breaking of the N-O bond and $^*\text{NO}_2$ stabilization.^[80] Overcoming these challenges will

support the rational design of MXene-based electrocatalysts with high activity and selectivity.

To this end, the following sections systematically discuss the key strategies employed to develop high-performance MXene-based electrocatalysts for NO_3^- RR, including heteroatom doping, heterostructure construction, bimetallic and alloyed particle anchoring, vacancy engineering, and MXene/organic-inorganic composites, each of which has demonstrated significant promise in enhancing catalytic activity and selectivity toward NH_3 generation.

4. In-situ and operando techniques of MXene-based materials

Over the past decade, growing interest in enhancing MXene features for various applications has created

significant demand for research into the MXene formation processes and the potential challenges they pose.^[82] In this way, conventional characterization techniques are frequently utilized to investigate the MXene-based catalysts. However, these ex-situ methods can solely track the conditions at the start or finish, as they are unable to observe the MXenes alterations and crucial intermediates in real-time throughout the reaction process.^[36, 83] Thus, it is essential to utilize in-situ characterization methods to fully analyze the interfacial structures of MXenes at the

atomic/nanoscale and understand their structure-performance correlations, which are fundamental to enhancing the rational design and practical use of MXene-based materials.^[84] Among numerous in-situ characterization techniques (Fig. 5), Fourier transform infrared spectroscopy (FTIR), X-Ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and X-ray absorption spectroscopy (XAS) are the most commonly used for MXene, each offering distinct capabilities for investigating specific properties or processes.^[40, 83, 85-87]

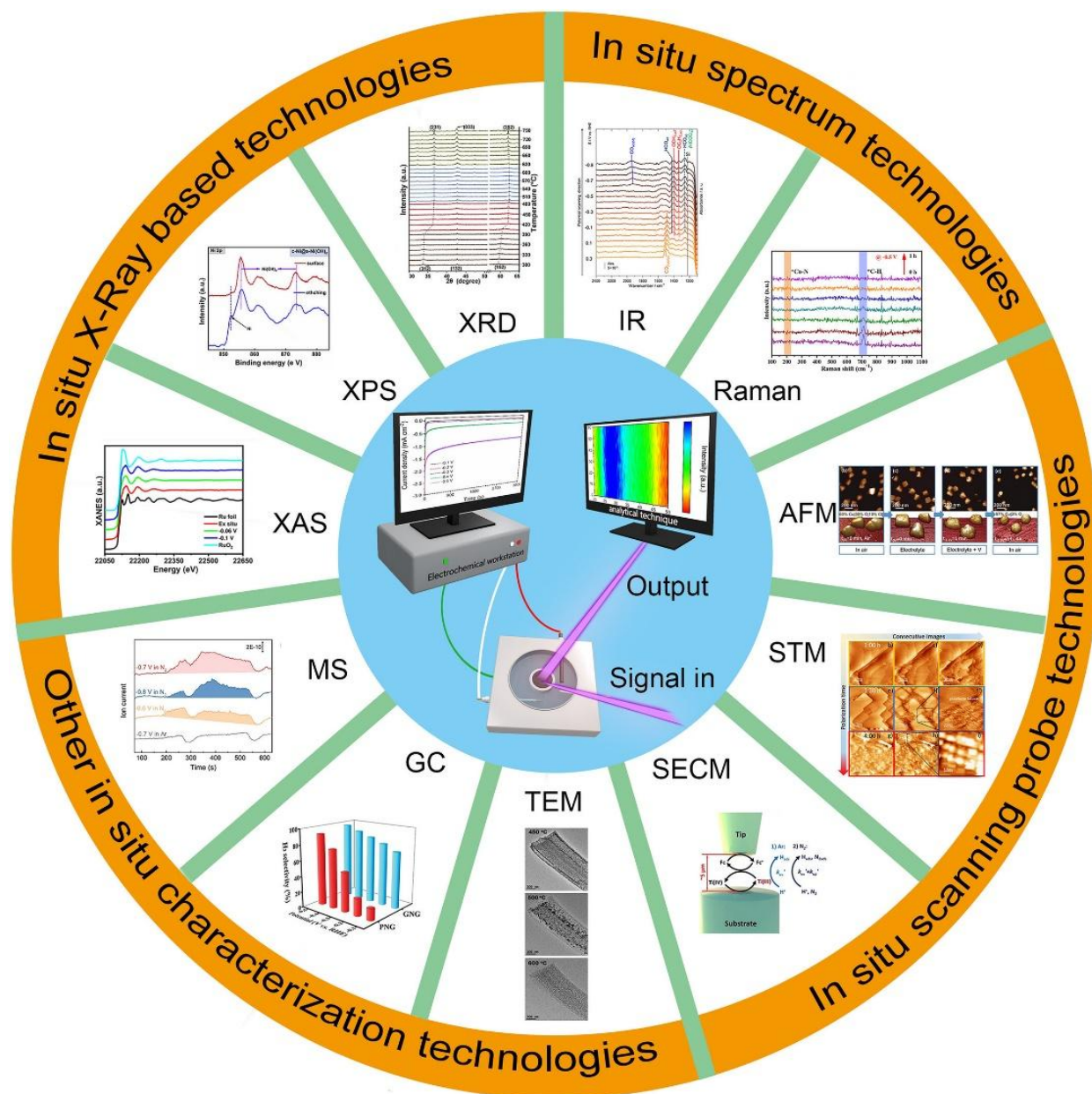


Figure 5. Applicable in-situ technologies for probing real-time variations of MXene-based catalysts, intermediates, and products.^[81] (Copyright 2022, Wiley)

4.1. FTIR

In general, infrared spectroscopy serves as an analytical technique to determine the molecular arrangement of materials and identify compounds by analyzing the relative oscillation and rotation of atoms within molecules.^[88, 89] By exciting bond vibrations and rotations in molecules, functional groups, and radicals, infrared spectroscopy can detect changes in dipole moment in the spectrum ($14300\text{--}14320\text{ cm}^{-1}$). Unlike other in-situ technologies, in-situ FTIR spectroscopy can emphasize identifying intermediates in catalytic reactions and offers benefits such as high sensitivity and rapid characterization, providing deeper insight into the catalytic mechanism.^[83] Specifically, in-situ FTIR can be employed to investigate the reaction mechanisms and interfacial processes taking place at the MXene-electrolyte boundary. This method highlights the complex interactions between water molecules and the MXene surface, distinguishing between different water environments and clarifying hydration and ion desolvation processes. In-situ FTIR enables a deeper understanding of the intricate interactions between the environment, the MXene surface, and the reaction processes occurring at the interface.^[90]

4.2. X-ray based methods

In general, X-rays are a type of electromagnetic radiation characterized by short wavelengths and high energy. Various phenomena, such as scattering and absorption, can be detected when X-rays interact with substances. X-ray analysis refers to analytical techniques that use X-rays as the radiation source. Based on various phenomena, it can be classified into three types: X-ray diffraction, X-ray photoelectron spectroscopy, and X-ray absorption spectroscopy. Each of them serves a purpose in the quantitative or qualitative evaluation of MXene-based materials. Notably, the emergence of the high-energy synchrotron's third generation has introduced ultra-high-brightness, high-energy X-rays, offering significant benefits for in-situ examinations of MXene reactions.^[83]

4.2.1. XRD

In this analysis technique, when a monochromatic X-ray strikes a crystal, the spacing between atoms is comparable to the wavelength of the incoming X-ray, causing scattered X-rays from various atoms to interfere and produce pronounced diffraction in certain directions.^[91, 92] The orientation and intensity of

diffraction lines in space are tightly linked to the crystal structure. Therefore, XRD can quantitatively and qualitatively analyze the average grain size, crystallinity, strain, and crystal defects of catalysts in electrochemical reduction reactions.^[83] Specifically, in-situ XRD has enabled structural examinations of MXene during chemical reactions or processing. For instance, in-situ XRD of the $\text{Ti}_3\text{C}_2\text{T}_x$ electrode in a KOH-containing electrolyte revealed minimal variation in the c-LP value of $0.33\text{ \AA}$ during electrochemical cycling (-1 to -0.2 V). A straightforward explanation is that the positively charged ions incorporated into $\text{Ti}_3\text{C}_2\text{T}_x$ enhance interlayer electrostatic attraction.^[93] Moreover, this method has further aided the examination of MXene-based composites^[94] by showing that c-LP varies after assembly, with increases indicating different MXene-additive stacking and/or a more uniform distribution of MXene sheets.^[93] In summary, while in-situ XRD offers straightforward access, sample preparation, and quick testing, it lacks the sensitivity to detect subtle chemical and/or structural changes in MXene sheets. For instance, XRD cannot detect the initial oxidation phases that occur at the MXene edge.^[93]

4.2.2. XPS

This technique is widely used in materials research, providing valuable information about electronic structure, and advances in advanced XPS methods, such as in-situ XPS, enable more comprehensive investigation of catalytic materials' properties.^[95] In-situ XPS is a highly surface-sensitive method to acquire an elemental distribution, oxidation states, and bonding context of materials.^[96] Recently, it has become a preferred technique for MXenes, even with persistent debates regarding spectral analysis;^[97] however, the need for ultrahigh vacuum (UHV) conditions in traditional XPS has limited its in-situ or operando use for observing catalytic processes.^[98] Other significant issue with in-situ XPS is that adventitious carbon (from the environment) on the surface renders the quantification of carbide and surface terminal groups inconsistent.^[97] Notably, ambient-pressure XPS based on synchrotron technology, with differential pumping stages, overcomes this limitation and enables surface analysis of electrocatalysts under near-operando conditions.^[98]

4.2.3. XAS

X-ray absorption spectroscopy is an element-specific method that demonstrates high sensitivity to surface chemistry.^[99] During XAS characterization, high-energy electrons excite an atom's inner-shell electrons

into vacant outer-shell orbitals involved in bonding, and the excess energy ultimately drives oscillations in the signal. Thus, the absorption edge in the XAS spectrum shows a feature associated with both the central atom and the coordinating atom.^[100] Because MXenes form with transition metals, nonmetal elements such as C or N, and surface terminations including O, F, etc., XAS at low photon energy is an ideal method for investigating their structure. The relative photon energy typically remains under 1000 eV, referred to as soft X-ray; XAS involves exciting electrons from core levels to partially filled and empty states.^[101, 102] A major benefit of XAS over traditional X-ray spectroscopic methods such as XPS is its ability to show changes in transition-metal oxidation states in-situ during chemical and electrochemical reactions.^[93] In addition, XAS is a powerful technique for probing the reaction mechanism of various metal oxides by tracking changes in the metal edge position during catalytic cycling.^[103] Accordingly, this method has been used to investigate vanadium oxidation-state variations in V_2CT_x (≈ 0.4 eV) during Na-ion battery cycling. This study showed that XAS can determine Ti oxidation-state changes in MXene when molecules like urea are intercalated (known as u- $Ti_3C_2T_x$). After urea intercalation, most Ti atoms showed an oxidation state near Ti^{4+} compared with unaltered $Ti_3C_2T_x$.^[104] Despite growing interest in XAS, it has not reached the same level of popularity as XPS or XRD because it typically requires synchrotron radiation to produce the necessary X-ray intensity.^[93]

5. Developed MXene-based electrocatalysts for NO_3^- RR

5.1. Mono-metallic-anchored MXene

Recently, many studies have reported the high electrocatalytic performance of MXene materials and their potential for ambient ammonia synthesis via eNO_3^- RR, particularly when exposed metal atoms are present.^[105] However, bare 2D MXenes are typically terminated with inactive $-F$ and $-OH$ functional groups, which mask the active metal centers that initiate reactions, thereby significantly reducing their catalytic activity.^[106, 107] To overcome this limitation, heteroatom metal doping has been employed as an effective strategy to enhance MXene performance and improve ammonia production efficiency.^[22] Accordingly, Chen *et al.*^[108] prepared Co-doped Ti_3C_2 MXene (Co- Ti_3C_2) via a straightforward hydrothermal

method, in which $CoCl_2 \cdot 6H_2O$ was incorporated into a Ti_3C_2 suspension at $180^\circ C$ for 24 h, yielding a composite with Co atoms uniformly embedded within the preserved layered MXene architecture. The retention of characteristic (002), (004), and (100) Ti_3C_2 diffraction planes in XRD patterns (**Fig. 6a**), alongside the appearance of Co-associated peaks at 25.2° and 27.3° , confirmed successful doping without structural disruption, while scanning electron microscopy (SEM) imaging (**Fig. 6b**) revealed evenly distributed bright spots across the nanosheet surface attributable to Co incorporation, and high-resolution TEM (HR-TEM) (**Fig. 6c**) resolved a characteristic (002) lattice spacing of 1.15 nm. XPS analysis (**Figs. 6d**) substantiated the Co- Ti_3C_2 bonding environment, with post-doping binding-energy shift in the Ti 2p spectra, notably a leftward shift consistent with increased electron density, collectively indicating successful Co integration and charge redistribution within the composite framework. Electrochemically, Co- Ti_3C_2 outperformed pristine Ti_3C_2 across all tested potentials, achieving a maximum NH_3 yield of $208.5 \text{ mg h}^{-1} \text{ mg}^{-1}$ with 66.8% Faradaic efficiency at -0.95 V vs. RHE (reversible hydrogen electrode) (**Fig. 6e**), and maintaining a notable yield of $158.9 \text{ mg h}^{-1} \text{ mg}^{-1}$ with 50.9% FE and a Tafel slope of $102.06 \text{ mV dec}^{-1}$ at -0.55 V vs. RHE, markedly lower than Ti_3C_2 's 173 mV dec^{-1} , reflecting substantially accelerated reaction kinetics (**Fig. 6f**). Chronoamperometric stability tests confirmed stable current density over 2 h (**Fig. 6g**), while five consecutive CV cycles demonstrated negligible performance attenuation (**Fig. 6h**). The nitrogen source was unambiguously validated by proton nuclear magnetic resonance (^1H NMR) isotope labeling with $^{14}N_2$, $^{15}N_2$, and Ar feed gases (**Fig. 6i**), confirming that NH_3 originated exclusively from nitrate rather than from environmental contamination. DFT free energy calculations comparing three proposed mechanistic pathways, direct dissociation, indirect dissociation, and hydrogen-assisted dissociation, revealed the direct pathway to be thermodynamically most favorable, with the rate-determining step of NO_3^- adsorption carrying the lowest energy barrier of 5.18 eV and an adsorption energy of 1.64 eV (**Fig. 6j**), while the hydrogen-assisted mechanism exhibited a substantially higher barrier of 11.27 eV. Critically, the HER energy barrier on Co- Ti_3C_2 (1.25 eV) exceeded that on bare Ti_3C_2 (0.92 eV), demonstrating that Co doping not only enhances nitrate adsorption and activation but also suppresses the competing hydrogen evolution pathway, thereby establishing Co- Ti_3C_2 as a promising and stable MXene-based electrocatalyst for selective nitrate-to-ammonia conversion.

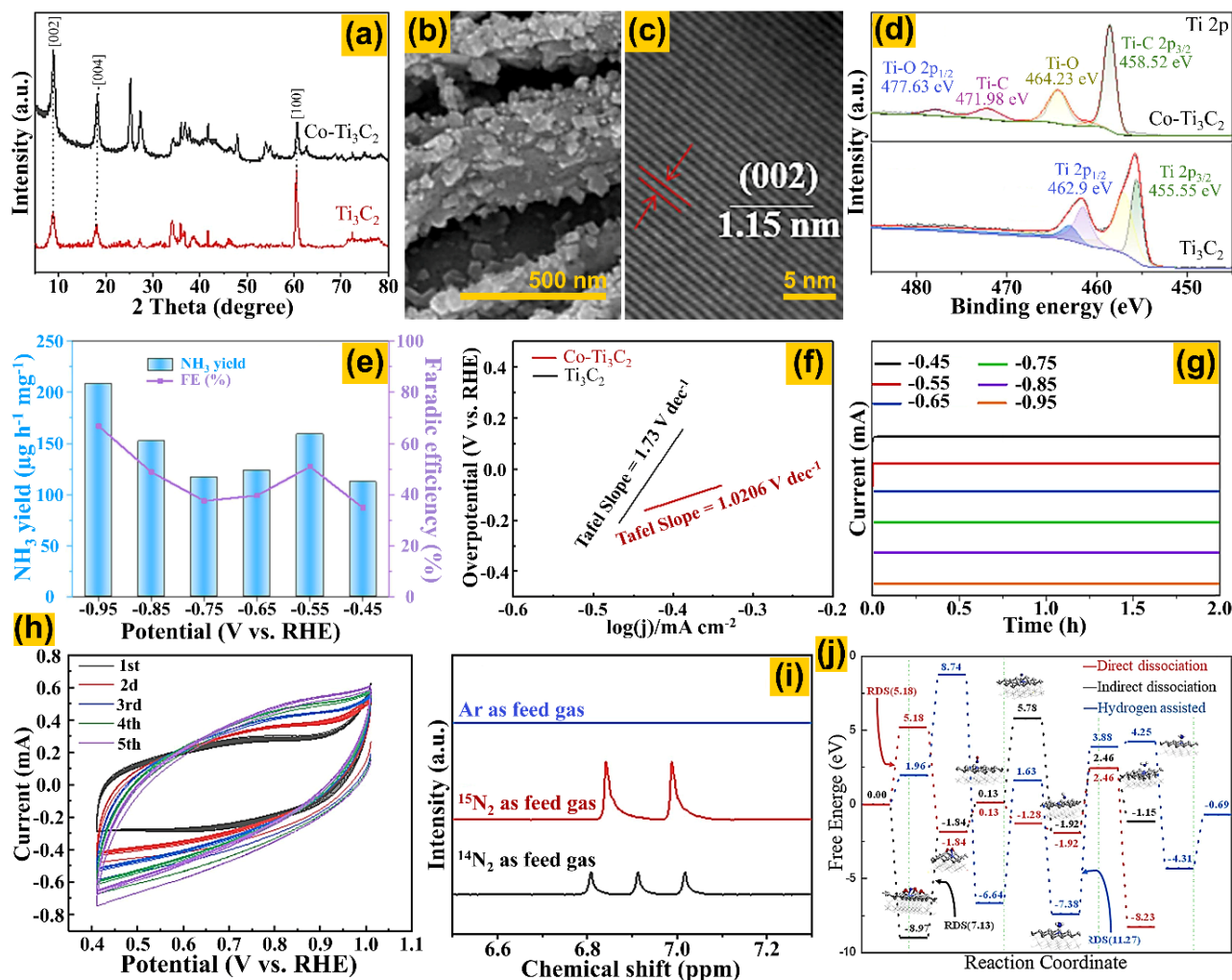


Figure 6. (a) XRD patterns of Co-Ti₃C₂ and Ti₃C₂. (b) SEM and (c) HR-TEM images of Co-Ti₃C₂. (d) XPS narrow scan of Ti 2p for Co-Ti₃C₂ and Ti₃C₂ samples. (e) Ammonia production rate and FE of Co-Ti₃C₂ at -0.95 V to -0.45 V. (f) Tafel slope plot for Co-Ti₃C₂ and Ti₃C₂. (g) I-t curves at various potentials and (h) Total scan of 5 CV curves for Co-Ti₃C₂ catalyst. (i) ¹H NMR measurements using ¹⁴N₂, ¹⁵N₂ and Ar as feed gases. (j) Comparison of the adsorption energy of HER catalytic activity.^[108] (Copyright 2024, Elsevier)

5.2. Mono-metallic-anchored/vacancy-engineered MXene

Recently, Cu-based catalysts have been developed for eNO₃-RR, achieving a high FE of over 90% in ammonia production. Copper is highly susceptible to oxidation under ambient conditions, readily forming surface oxide layers. Despite this, the influence of Cu's oxidation state on the electrocatalytic activity and selectivity toward NH₃ production during eNO₃-RR remains insufficiently understood.^[15] It was reported that integrating Cu particles into the MXene structure not only enhances active-site availability and electronic modulation but also significantly boosts overall catalytic efficiency and selectivity in ammonia

synthesis.^[75]

On the other hand, in multilayer MXenes, strong interlayer interactions between the M and X layers persist, leading to the progressive collapse of the characteristic lamellar structure. This structural degradation significantly reduces the accessible active surface area of the MXene, thereby limiting its electrochemical performance.^[109] To overcome this intrinsic limitation, the strategic formation of vacancies has emerged as a highly effective modification approach. This strategy significantly modulates the electronic properties of catalysts and optimizes the adsorption energy of reactive species, thereby enhancing catalytic performance relative to their pristine counterparts.^[5, 110] Among various types of

defects, surface oxygen vacancies (O_{vs}) have attracted particular attention due to their ability to activate adsorbates and trap charge carriers, thereby significantly enhancing catalytic efficiency.^[111,112]

In this manner, Tan *et al.*^[113] identified a previously underappreciated bottleneck in MXene-based eNO_3^-RR , namely the tendency of pristine $Ti_3C_2T_x$ to release NO_2 intermediates as soluble NO_2^- byproducts rather than retaining them for further hydrogenation, and addressed it through the rational co-introduction of Cu species and oxygen vacancies onto the MXene surface, yielding a catalyst denoted $Cu@Ti_3C_2O_v$. The synthesis followed a sequential three-step protocol (**Fig. 7a**): $Ti_3C_2T_x$ was first thermally annealed in air, then reduced with $NaBH_4$ to generate the vacancy-rich $Ti_3C_2O_v$ intermediate, after which Cu^{2+} ions were deposited via impregnation-reduction to anchor atomically dispersed $Cu^{0/1+}$ species at a deliberately low loading of 1.48 wt%. Notably, despite the relatively high Cu loading (12.72 wt%, **Fig. 7b**), high-angle annular dark-field scanning TEM (HAADF-STEM) imaging (**Fig. 7c**) showed no evidence of Cu agglomeration, indicating that the Cu species remain atomically dispersed throughout the $Cu@Ti_3C_2O_v$. The electron paramagnetic resonance (EPR) spectroscopy at $g = 2.003$ (**Fig. 7d**) tracked the progressive creation of oxygen vacancies across the sample series, with Cu loading further amplifying the EPR signal intensity, rationalized by Cu withdrawing electrons from bonded surface O atoms to generate additional unpaired electrons at adjacent O sites. XPS O 1s and Ti 2p spectra (**Figs. 7e and f**) corroborated this picture: the bridging O fraction decreased from 43.6% in pristine $Ti_3C_2T_x$ to 32.2% in $Ti_3C_2O_v$, an additional Cu-O bond appeared at 531.0 eV in $Cu@Ti_3C_2O_v$, confirming vacancy enrichment and Cu-O surface coordination. Because FE_{NH_3} shows a declining trend with increasing Cu loading density (**Fig. 7g**), this suggests that an optimal Cu content synergizes with oxygen vacancies to enhance both FE_{NH_3} and NH_3 yield rates in the eNO_3^-RR . Electrochemically, the cooperative effect translated into a striking performance advantage: while $Ti_3C_2O_v$ already showed FE_{NH_3} values of 78.5–88.4% at -1.1 to -1.5 V vs. RHE alongside persistent NO_2^- byproduct FEs of 12.7–21.5%, $Cu@Ti_3C_2O_v$ achieved $FE_{NH_3} > 97.2\%$ across the entire potential window with a maximum NH_3 yield rate of $11,928.6 \mu g h^{-1} mg_{cat}^{-1}$. After 1 h reaction, 400 mg L^{-1} of NO_3^- is reduced to 285.2 ppm, corresponding to a NO_3^- removal ratio of 28.7% and virtually suppressed NO_2^- production ($S_{NO_2^-} = 5.2\%$, $S_{NH_3} = 91.0\%$ at -1.2 V with 400 ppm NO_3^-), as demonstrated in **Fig. 7h**. Isotope labeling with $^{15}NO_3^-$ confirmed exclusive NO_3^- -derived NH_4^+

production (**Fig. 7i**), and twelve consecutive cycling tests showed negligible attenuation of yield rate, FE, and current density (**Fig. 7j**). The mechanistic rationale for NO_2^- suppression was illuminated through DFT calculations. Charge density difference maps showed large electron clouds concentrated at the Cu- NO_3^- interface in $Cu@Ti_3C_2O_v$, compared with the Ti- NO_3^- interface in $Ti_3C_2O_v$ (**Fig. 7k**), while the projected density of states (PDOS) analysis revealed substantially stronger hybridization between Cu 3d and 2p orbits of the adsorbed NO_3^- than between Ti 3d and NO_3^- 2p states. These findings establish that Cu's energetically matched *d*-electrons enable more effective electron donation into the LUMO π^* orbital of NO_3^- , thereby suppressing NO_2^- accumulation and driving selectivity toward NH_3 . Gibbs free energy diagrams (**Fig. 7l**) further showed that $*NO_2$ desorption to form free NO_2^- faces a high barrier of 1.74 eV on $Cu@Ti_3C_2O_v$, far exceeding the barrier on $Ti_3C_2O_v$, while the subsequent rate-limiting $*NO \rightarrow *N$ step requires only 1.24 eV, and all downstream hydrogenation steps ($*N \rightarrow *NH \rightarrow *NH_2 \rightarrow *NH_3$) proceed spontaneously. These results provide a complete thermodynamic explanation for a synergistic effect between Cu and O vacancies, which strengthens the adsorption of $*NO_2$ and promotes the hydrogenation of $*N$, thereby enhancing FE_{NH_3} and NH_3 yield rates.

5.3. Bimetallic-anchored MXene

To address the inherent technical limitations of mono-metallic catalysts anchored on MXene supports, particular attention has been devoted to bimetallic and multimetallic alloys incorporating precious metals such as ruthenium (Ru), palladium (Pd), and silver (Ag), as well as non-precious transition-metal-based systems including Cu, Ni, Co, and iron (Fe).^[114–117] From this point of view, Sheng *et al.*^[118] developed bimetallic CuCo nanoparticles, in-situ grown on $Ti_3C_2T_x$ MXene nanosheets, to address the persistent challenge of Cu and Co nanoparticle agglomeration during the electrocatalytic NO_3^-RR for NH_3 synthesis. The MXene nanosheets were synthesized via selective etching of the Al atomic layer from Ti_3AlC_2 MAX phase, followed by LiCl-assisted delamination (**Fig. 8a**), yielding ultrathin few-layer nanosheets. As confirmed by HAADF-STEM imaging (**Figs. 8b and c**), the CuCo nanoclusters (~ 2 nm) were uniformly dispersed across the MXene substrate, thereby preventing agglomeration and maximizing active-site exposure. XPS analyses (**Figs. 8d and e**) verified the successful composite formation, identifying Cu^0/Cu^{2+} and Co^{2+}/Co^{3+} species alongside Ti_3C_2 MXene, with

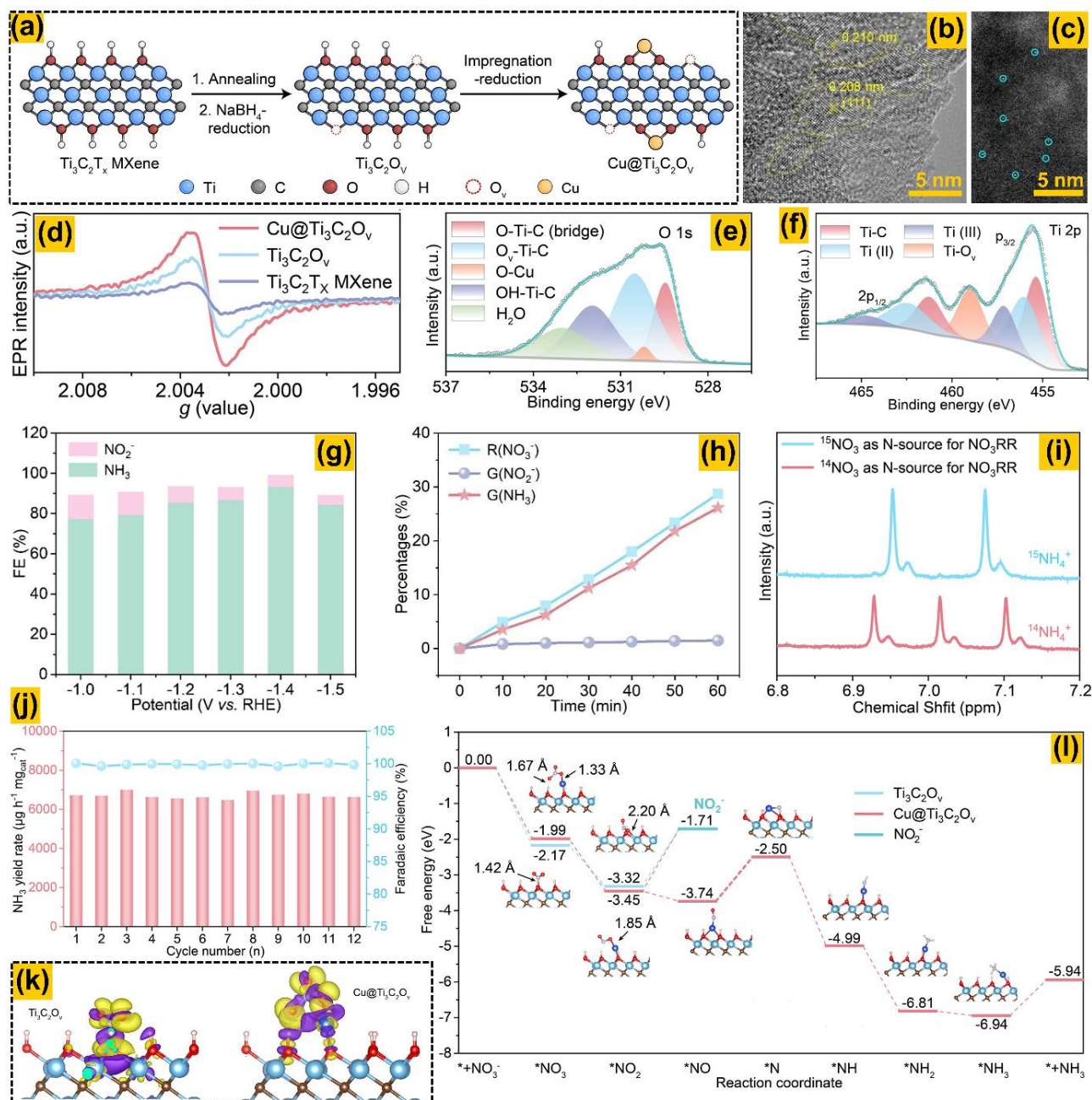


Figure 7. (a) Schematic illustration of the synthesis of Cu@Ti₃C₂O_v. (b) HR-TEM and (c) HAADF scanning TEM images of Cu@Ti₃C₂O_v. (d) EPR spectra of Cu@Ti₃C₂O_v, Ti₃C₂O_v, and Ti₃C₂T_x MXene. XPS spectra of (e) O 1s and (f) Ti 2p for Cu@Ti₃C₂O_v. (g) FE of NO₂⁻ and NH₃ of Cu@Ti₃C₂O_v with a high loading density of 12.72 wt%. (h) Percentages of NO₃⁻-N removal, NO₂⁻-N generation, and NH₃-N generation of Cu@Ti₃C₂O_v. (i) ¹H NMR spectra of Cu@Ti₃C₂O_v. (j) Cycling performance of Cu@Ti₃C₂O_v at -1.2 V versus RHE. (k) The charge density difference of adsorption on (left) Ti₃C₂O_v and (right) Cu@Ti₃C₂O_v. (l) The calculated Gibbs free energy diagrams and corresponding geometric structures. [113] (Copyright 2024, Wiley)

the leftward shift of the (002) diffraction peak confirming increased interlayer d-spacing upon metal loading. Among the series of Cu_xCo_y/MXene composites evaluated, Cu₂Co₁/MXene exhibited the

highest electrochemical double-layer capacitance (263.3 μF cm⁻²) (Fig. 8f), indicating the greatest density of exposed active sites, and delivered a superior ammonia production rate of 2.73 mg cm⁻² h⁻¹ with

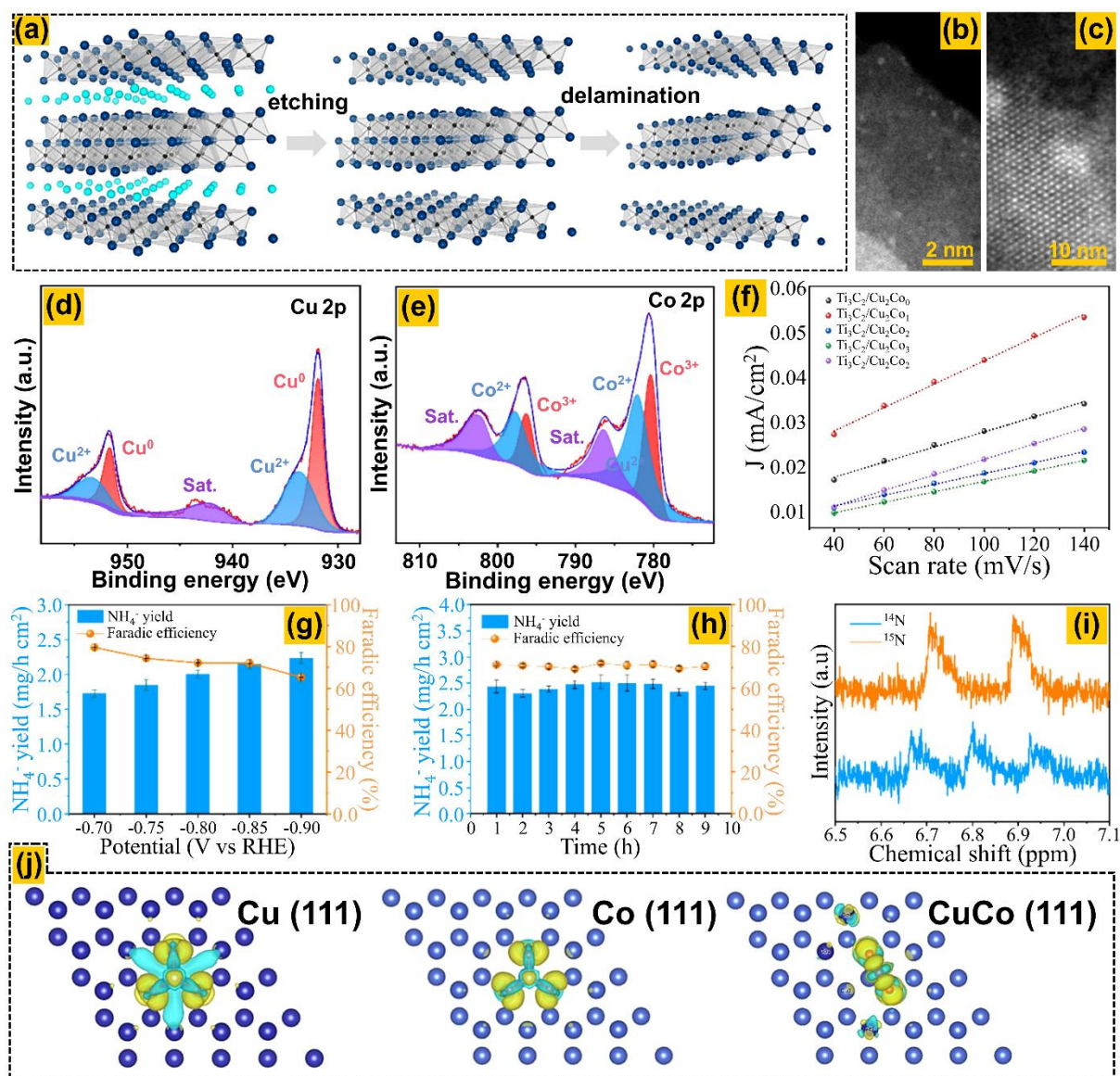


Figure 8. (a) Schematic illustration of the synthesis of $\text{Ti}_3\text{C}_2\text{MXene}$ via selective etching and delamination from the Ti_3AlC_2 MAX phase. (b) HAADF-STEM and (c) high-resolution HAADF-STEM images of $\text{Cu}_2\text{Co}_1/\text{MXene}$. XPS spectra of (d) Cu 2p and (e) Co 2p in the $\text{Cu}_2\text{Co}_1/\text{MXene}$ sample. (f) Plots of the current density vs. the scan rate for $\text{Cu}_x\text{Co}_y/\text{MXene}$ with different molar ratios. The ammonia yield rate and faradaic efficiency for ammonia (g) at different potentials and (h) over $\text{Cu}_2\text{Co}_1/\text{MXene}$ during the cycling stability test. (i) NMR spectra of electrocatalytic products with different nitrogen sources. (j) Electron transfer during nitro group adsorption.^[118] (Copyright 2026, Elsevier)

72.05% Faradaic efficiency and 90.6% selectivity at -0.85 V vs. RHE (**Fig. 8g**), alongside exceptional cycling durability over 9 h (**Fig. 8h**). Isotopic NMR labeling experiments (**Fig. 8i**) unambiguously confirmed NO_3^- as the exclusive nitrogen source for NH_4^+ production, ruling out any environmental contamination. DFT calculations revealed that the bimetallic $\text{Cu}_x\text{Co}_y(111)$ surface exhibits significantly

stronger adsorption energies for NO_3^- (-3.39 eV) and NO_2^- (-3.10 eV) than the monometallic Cu(111) (-1.73 eV) and Co(111) (-2.44 eV) surfaces. Meanwhile, differential charge density analysis and d -band center calculations further confirmed the highest net charge transfer to the nitro group on CuCo(111) (**Fig. 8j**), which is attributed to the upward shift of the Co d -band center toward the Fermi level. The

synergistic catalytic mechanism involves Cu sites preferentially adsorbing and activating nitrate ions, while Co facilitates protonation, electron transfer, and the further reduction of nitrite to ammonia, collectively lowering the overall energy barrier for ammonia formation and establishing $\text{Cu}_2\text{Co}_1/\text{MXene}$ as a benchmark electrocatalyst for sustainable nitrogen-cycle transformation.

In another study, Sun *et al.* [116] fabricated a Pd-Cu bimetal functionalized $\text{Ti}_3\text{C}_2\text{T}_x$ MXene laminar membrane operating in flow-through electrofiltration mode to overcome the sluggish mass transfer that fundamentally limits conventional electrocatalytic NO_3^- -RR systems. The membrane was constructed via vacuum filtration of a NaBH_4 -reduced Pd-Cu/MXene suspension onto a poly (vinylidene fluoride) (PVDF) substrate, yielding an accordion-like multilayer architecture ($\sim 114 \mu\text{m}$ thick, **Fig. 9a**) with Pd and Cu nanoparticles (~ 30 -50 nm, **Figs. 9b** and **c**) uniformly embedded within the MXene interlayer nanochannels, as confirmed by SEM analysis (**Fig. 9d**). XRD and XPS analyses verified that Pd^0 and Cu^0 were the predominant valence states on the membrane surface, with a sheet resistance of $12.08 \Omega \text{ sq}^{-1}$ reflecting excellent electrical conductivity. Systematic optimization of the Pd:Cu ratio, Pd-Cu:MXene loading, and total membrane dosage identified a Pd:Cu ratio of 5:5 (**Fig. 9e**) and Pd-Cu:MXene ratio of $0.03 \text{ mmol mg}^{-1}$ as optimal (**Fig. 9f**). Despite the presence of dissolved oxygen (DO), the Pd-Cu/MXene membrane demonstrated exceptional nitrate reduction performance with $\sim 99\%$ NO_3^- -N removal efficiency and only a marginal 4% decrease in NH_4^+ -N selectivity (from $74.1 \pm 0.6\%$ to $71.1 \pm 1.2\%$), confirming that the oxygen reduction reaction could not compete with eNO_3^- -RR on this membrane (**Fig. 9g**). It was assumed that hydrogen bubbles generated by the HER could block active sites or structurally damage the laminar membrane during long-term operation. Accordingly, XPS analysis before and after 24 h of continuous operation confirmed that Cu^0 and Pd^0 remained the dominant surface species despite slight decreases in peak intensities (**Figs. 9h** and **i**), collectively demonstrating that the Pd-Cu/MXene laminar membrane retained excellent chemical stability, stable product selectivity, and relatively consistent NO_3^- -reduction performance over extended operation. Crucially, the electrochemical filtration mode delivered an NO_3^- -N removal rate 11 times greater than that of the batch system without filtration, attributable to a 13-fold enhancement in the mass transfer constant (km : 0.13 vs. 0.01 m h^{-1}) (**Fig. 9j**) alongside an increased electrochemical active area (ECSA) from 1.77 to 2.27

m^2 . The filtration configuration also suppressed NH_4^+ re-oxidation at the anode by directing produced NH_4^+ away from the Pt counter electrode before contact, boosting NH_4^+ -N selectivity from 21.9% in the unfiltered batch system to 67.0%. TBA quenching experiments and EPR spectroscopy revealed that direct electron transfer was the dominant reduction mechanism (contributing $\sim 79.4\%$), as atomic $\cdot\text{H}$ was strongly adsorbed on the membrane surface rather than participating freely in solution-phase reduction (**Fig. 9k**). DFT free energy calculations mechanistically clarified the complementary roles of Cu and Pd: Cu sites preferentially adsorb NO_3^- (-2.91 eV) and facilitate its reduction to $\cdot\text{NO}_2$ as well as subsequent hydrogenation to NH_3 , while Pd sites catalyze the critical deoxygenation of $\cdot\text{NO}_2$ to $\cdot\text{NO}$ (-2.76 eV), with their synergistic interplay collectively lowering the overall energy barriers for the NO_3^- -to- NH_4^+ conversion pathway (**Fig. 9l**).

Moreover, Abbott *et al.* [119] drew direct inspiration from the dual-metal enzymatic machinery of natural nitrate reductase (NRase) and cytochrome c nitrite reductase (NrfA) enzymes, in which Mo and Fe centers sequentially catalyze the eight-electron conversion of nitrate to ammonium. The conceptual parallel between the natural enzymatic mechanism and the proposed MXene pathway is captured in **Fig. 10a**, where successive proton-coupled electron transfer (PCET) steps reduce surface oxo T_x -containing groups to generate coordinatively unsaturated Mo vacancy sites (Mo-V_O) that subsequently bind and activate the nitrate substrate via oxygen atom transfer, directly echoing the $\text{Mo}^{\text{VI}}/\text{Mo}^{\text{IV}}$ redox cycle of NRases. A surface-functionalized, Fe-doped MXene, $\text{Mo}_2\text{CT}_x:\text{Fe}$ ($\text{T}_x = -\text{O}, -\text{OH}, -\text{F}$) (**Fig. 10b**), was synthesized, wherein atomically dispersed Fe dopants substitute Mo sites within the Mo_2CT_x lattice framework (**Fig. 10c**). Electrochemically, $\text{Mo}_2\text{CT}_x:\text{Fe}$ consistently outperformed the unsubstituted Mo_2CT_x across both acidic and neutral media; in acidic conditions ($0.05 \text{ M H}_2\text{SO}_4$), $\text{Mo}_2\text{CT}_x:\text{Fe}$ reached a peak FE_{NH_3} of 41% and an NH_3 yield rate of $3.2 \mu\text{mol h}^{-1} \text{ mg}^{-1}$ at $-0.2 \text{ V}_{\text{RHE}}$ (**Fig. 10d**), nearly double the FE and more than twice the yield rate of Mo_2CT_x , while switching to neutral media ($0.5 \text{ M Na}_2\text{SO}_4$) elevated performance substantially, achieving 70% FE_{NH_3} and $12.9 \mu\text{mol h}^{-1} \text{ mg}^{-1}$ at $-0.6 \text{ V}_{\text{RHE}}$, as shown in **Fig. 10e**. The nitrogen origin was unambiguously confirmed by $^{15}\text{NO}_3^-$ isotope labeling, with ^1H NMR spectra showing the expected doublet for $^{15}\text{NH}_4^+$ alongside the triplet for $^{14}\text{NH}_4^+$. The catalyst's practical relevance was further demonstrated by selectively reducing nitrate from contaminated tap water at environmentally relevant

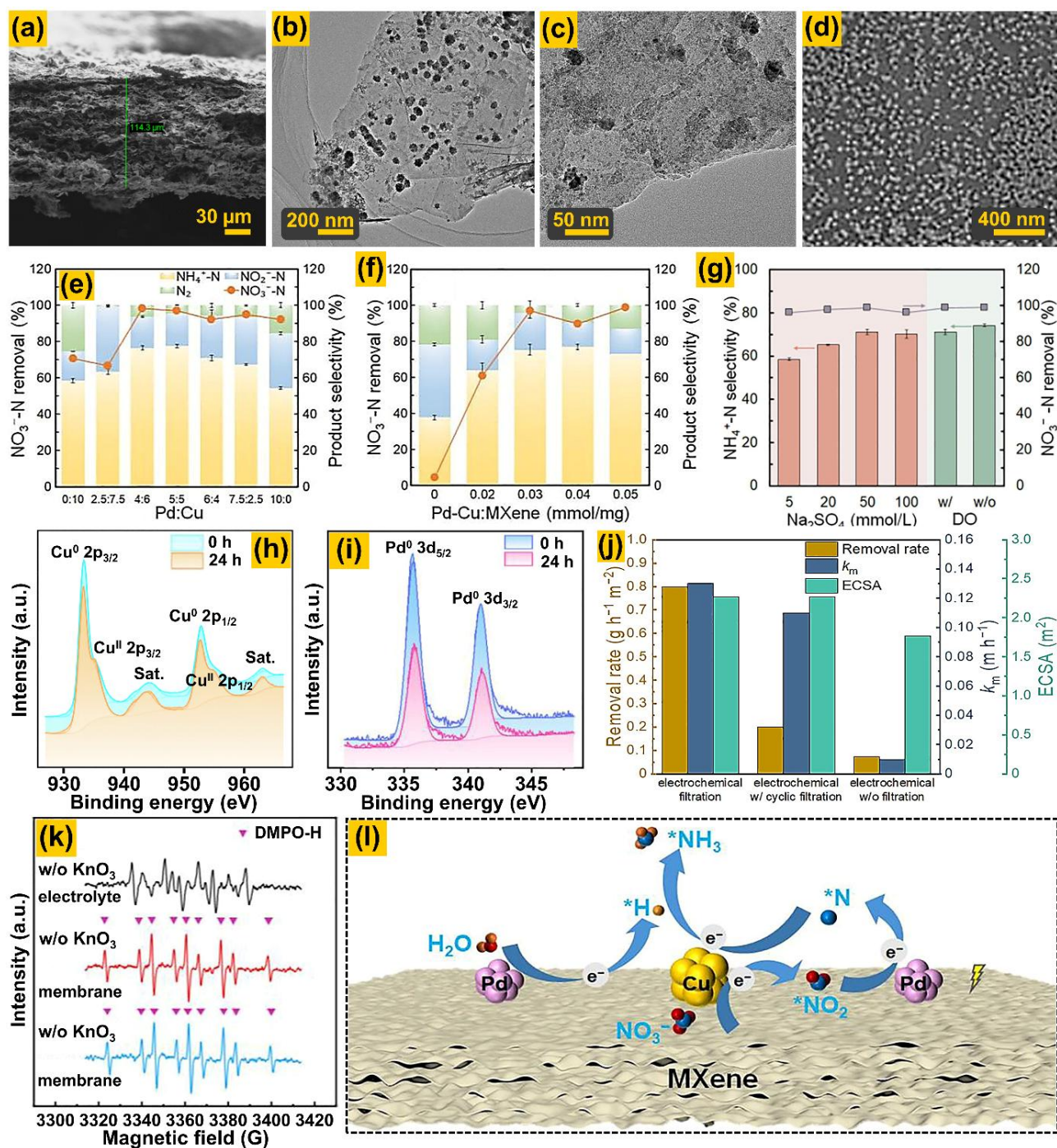


Figure 9. (a) Cross-sectional SEM, (b, c) TEM, and (d) surface SEM images of the Pd-Cu/MXene laminar membrane. NO_3^- -N removal efficiency and product selectivity at various (e) Pd:Cu ratios and (f) Pd-Cu:MXene ratios. (Solution: $20 \text{ mg L}^{-1} \text{NO}_3^-$ -N and $50 \text{ mmol L}^{-1} \text{Na}_2\text{SO}_4$; Potential: -0.9 V vs. SCE ; Membrane flux: $40 \text{ L m}^{-2} \text{h}^{-1}$). (g) NO_3^- -N removal efficiency and NH_4^+ -N selectivity at different Na_2SO_4 concentrations, with and without DO. (h) Cu 2p and (i) Pd 3d XPS spectra before and after continuous running for 24 h. (j) NO_3^- -N removal rate, k_m , and ECSA of the Pd-Cu/MXene laminar membrane in the electrochemical system with filtration, cyclic filtration, and without filtration, respectively. (k) EPR spectra of catholyte or the Pd-Cu/MXene sheets in the H-type reactor (solution without KNO_3 : $50 \text{ mmol L}^{-1} \text{Na}_2\text{SO}_4$; Solution with KNO_3 : $20 \text{ mg L}^{-1} \text{NO}_3^-$ -N and $50 \text{ mmol L}^{-1} \text{Na}_2\text{SO}_4$). (l) Mechanism illustration of electrocatalytic nitrate reduction on Pd-Cu/MXene laminar membrane.^[116] (Copyright 2025, Elsevier)

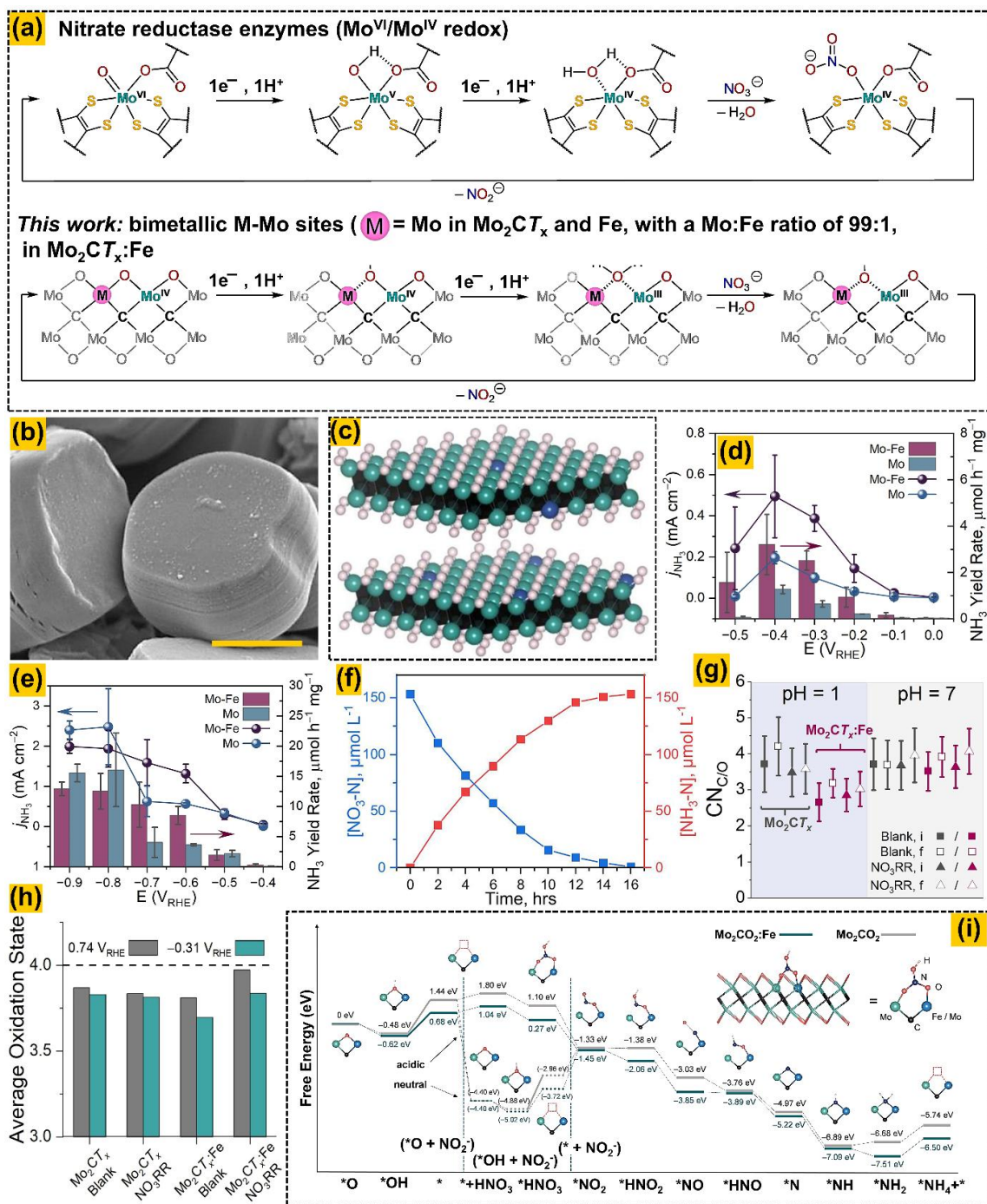


Figure 10. (a) Proposed NO₃RR mechanism for (up) natural nitrate reductases and (down) the MXene materials studied in this work (Charges are omitted for brevity). (b) SEM image and (c) a representation of Mo₂CT_x:Fe. Partial current densities for NH₃ and the NH₃ yield rates at each CA potential in (d) 0.05 M H₂SO₄ and (e) 0.5 M Na₂SO₄. (f) Time-dependent changes in the concentrations of NO₃-N and NH₃-N over Mo₂CT_x:Fe at -0.4 V_{RHE}. (g) Mo-O/C coordination numbers as determined from fitting the FT-EXAFS data (Black symbols indicate the fitting results for Mo₂CT_x, and red symbols indicate those for Mo₂CT_x:Fe. As specified in the Figure legend, square symbols (■) are under blank conditions (0 mM NO₃⁻) and triangle symbols (▲) are under NO₃RR conditions (100 mM NO₃⁻). Filled symbols (e.g. ■) indicate the initial potential (i.e., OCP), and empty symbols (e.g. □) are the final potential where NO₃⁻RR occurs. (h) Oxidation state of Mo₂CT_x:Fe and Mo₂CT_x at the initial (0.74 V_{RHE}) and final (-0.31 V_{RHE}) applied potentials in 0.5 M Na₂SO₄. (i) DFT-calculated free energy reaction pathways for the NO₃RR on Mo₂CO₂ and Mo₂CO₂:Fe catalysts in acidic and neutral media.^[119] (Copyright 2023, Wiley)

concentrations ($10 \text{ mg L}^{-1} \text{ NO}_3\text{-N}$, i.e. $44.3 \text{ mg L}^{-1} \text{ NO}_3^-$), achieving 70% FE_{NH_3} and complete nitrate conversion within 16 h (**Fig. 10f**). The mechanistic origin of Fe's promotional role was interrogated through in-situ Mo K-edge X-ray absorption spectroscopy, which revealed that under blank electrochemical conditions $\text{Mo}_2\text{CT}_x\text{:Fe}$ undergoes a more pronounced reduction of Mo centers (from +4 to approximately +3.4) (**Fig. 10g**) than Mo_2CT_x (from +4 to +3.8) (**Fig. 10h**). Under NO_3^- -RR conditions, the Mo oxidation state remains stable in both materials, indicating that incoming nitrate acts as an oxidant, filling the transiently formed T_x vacancies via O^* transfer. Fourier transform of X-ray absorption fine structure (FT-EXAFS) fitting further confirmed that $\text{Mo}_2\text{CT}_x\text{:Fe}$ exhibits a persistently lower Mo-O/C coordination number and a lower Mo-Mo coordination number than Mo_2CT_x under all conditions examined, indicating a more disordered MXene surface with a higher intrinsic fraction of under-coordinated Mo sites. DFT free energy calculations (**Fig. 10i**) completed the mechanistic picture: in acidic media, the rate-limiting step is oxygen vacancy formation ($^*\text{OH} \rightarrow ^*$), and this step is less endergonic on the Fe-substituted surface, consistent with the XAS observations; in neutral media, while the O-vacancy formation barrier is comparable across both surfaces, the presence of Fe shifts the limiting step to NO_2^- adsorption rather than vacancy formation, highlighting that Fe facilitates T_x vacancy generation through distinct pH-dependent mechanisms, and that these surface vacancies serve as the critical active sites for nitrate binding and conversion in close analogy to the terminal oxo site of natural Mo-based nitrate reductase enzymes.

5.4. Bimetallic-anchored/vacancy-engineered MXene

As mentioned in Section 5.2, creating vacancies in MXene nanosheets has emerged as a highly effective strategy to enhance their electrocatalytic performance in nitrate reduction. Recent studies have demonstrated that introducing vacancies significantly enhances the selectivity and overall efficiency of MXene-based catalysts.^[120] In addition, according to the reported results in Section 4.3, it is anticipated that the immobilization of bimetallic or alloyed clusters on MXene will not only preserve the exceptional physicochemical properties of the MXene supports, such as their high electrical conductivity, large surface area, and tunable surface chemistry, but also unlock synergistic effects between the metallic clusters and the MXene matrix.^[79] From this perspective, Ma *et al.*^[117]

engineered a wrinkled, three-dimensional (3D)-structured, N-doped $\text{Ti}_3\text{C}_2\text{T}_x$ MXene with enriched oxygen vacancies to anchor CuNi alloy nanoparticles via metal-support interactions (MSI) and to address the dual challenges of nanoparticle agglomeration and sluggish nitrate reduction kinetics. Melamine-formaldehyde spheres (MFs) were strategically employed as self-sacrificial nitrogen source templates that, upon H_2/Ar (10 % H_2) annealing at 400°C , simultaneously induced a crumpled 3D morphology, introduced abundant surface oxygen vacancies, and facilitated in-situ CuNi alloy anchoring via stable Ti-O-M bridging bonds as schematically captured in **Fig. 11a**. For better understanding, in this procedure, negatively charged $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets were combined with positively charged MFs via electrostatic self-assembly, yielding the MFs- $\text{Ti}_3\text{C}_2\text{T}_x$ composite (**Fig. 11b**), and annealing of the MFs- $\text{Ti}_3\text{C}_2\text{T}_x$ sample afforded nitrogen-doped $\text{Ti}_3\text{C}_2\text{T}_x$ (N- $\text{Ti}_3\text{C}_2\text{T}_x$) (**Fig. 11c**). Structural confirmation came from HR-TEM imaging revealing CuNi (111) and (200) lattice fringes of 0.206 and 0.178 nm, respectively, alongside the $\text{Ti}_{0.72}\text{O}_2$ (101) plane at 0.351 nm (**Figs. 11d and e**), while EPR spectroscopy at $g = 2.003$ unambiguously verified the elevated oxygen vacancy concentration introduced by MFs intercalation (**Fig. 11f**). XPS analysis disclosed a reciprocal binding energy shift between Cu (-0.1 eV) and Ni ($+0.5 \text{ eV}$) in $\text{Cu}_5\text{Ni}_5/\text{N-Ti}_3\text{C}_2\text{T}_x$ relative to their monometallic counterparts, confirming Ni-to-Cu electron donation and the establishment of charge redistribution within the Ti-O-M framework. Among all Cu_xNi_y compositions evaluated, $\text{Cu}_5\text{Ni}_5/\text{N-Ti}_3\text{C}_2\text{T}_x$ delivered the highest double-layer capacitance ($C_{\text{dl}} = 1.47 \text{ mF cm}^{-2}$) (**Fig. 11g**) and the lowest charge transfer resistance (8.04Ω) (**Fig. 11h**), translating into a peak Faradaic efficiency of 97.50% at -0.27 V vs. RHE and a maximum NH_3 yield rate of $527.44 \mu\text{mol h}^{-1} \text{ cm}^{-2}$ at -0.37 V vs. RHE, dramatically outperforming the monometallic Cu/N- $\text{Ti}_3\text{C}_2\text{T}_x$ ($23.83 \mu\text{mol h}^{-1} \text{ cm}^{-2}$) and Ni/N- $\text{Ti}_3\text{C}_2\text{T}_x$ ($25.07 \mu\text{mol h}^{-1} \text{ cm}^{-2}$) counterparts, as demonstrated in **Fig. 11i**. ^{15}N isotopic NMR labeling (**Fig. 11j**) unambiguously confirmed NO_3^- as the exclusive nitrogen source. In-situ electrochemical Raman spectroscopy tracked the sequential appearance and disappearance of NO_2^- , NO_3^- , and NH_3 vibrational bands as a function of applied potential, while EPR measurements using 5, 5-dimethyl-1-pyrroline N-oxide (DMPO) as a radical trap confirmed that Ni sites are primarily responsible for $^*\text{H}$ generation, which is subsequently consumed during NRA intermediates rather than recombining to H_2 . DFT free energy calculations (**Figs. 11k and l**) further revealed that the

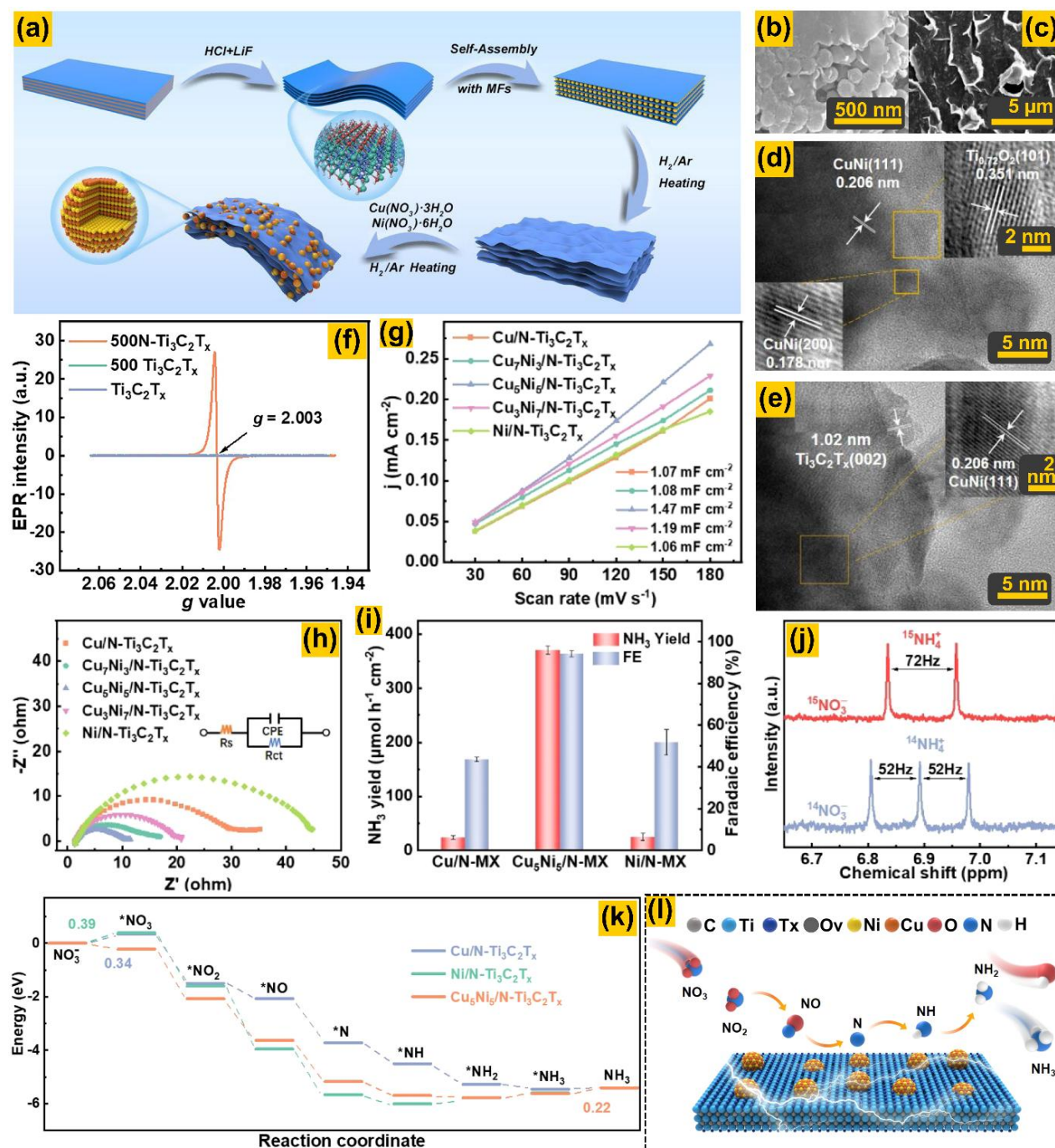


Figure 11. (a) Schematic sketch of the fabrication of the $\text{Cu}_x\text{Ni}_y/\text{N-Ti}_3\text{C}_2\text{T}_x$ catalyst. The field emission scanning electron microscope (FE-SEM) images of (b) MFs- $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets and (c) N- $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets. (d, e) HR-TEM images of $\text{Cu}_5\text{Ni}_5/\text{N-Ti}_3\text{C}_2\text{T}_x$. (f) EPR spectra of 500N- $\text{Ti}_3\text{C}_2\text{T}_x$, 500 $\text{Ti}_3\text{C}_2\text{T}_x$, and $\text{Ti}_3\text{C}_2\text{T}_x$. (g) C_d values at different scanning rates. (h) EIS spectra of $\text{Cu}_x\text{Ni}_y/\text{N-Ti}_3\text{C}_2\text{T}_x$. (i) NH_3 yield rates and FE for the catalysts of $\text{Cu/N-Ti}_3\text{C}_2\text{T}_x$, $\text{Cu}_5\text{Ni}_5/\text{N-Ti}_3\text{C}_2\text{T}_x$, and $\text{Ni/N-Ti}_3\text{C}_2\text{T}_x$ at -0.27 V. (j) ^1H NMR spectra of the electrolyte performed by $\text{Cu}_5\text{Ni}_5/\text{N-Ti}_3\text{C}_2\text{T}_x$. (k) Free energies for NRA on $\text{Cu}_5\text{Ni}_5/\text{N-Ti}_3\text{C}_2\text{T}_x$, $\text{Ni/N-Ti}_3\text{C}_2\text{T}_x$, and $\text{Cu/N-Ti}_3\text{C}_2\text{T}_x$, respectively. (l) The proposed pathway of NRA over $\text{Cu}_5\text{Ni}_5/\text{N-Ti}_3\text{C}_2\text{T}_x$.^[117] (Copyright 2025, Elsevier)

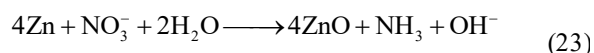
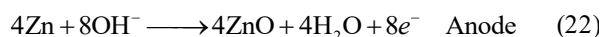
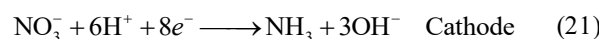
upward shift of the d-band center in $\text{Cu}_5\text{Ni}_5/\text{N-Ti}_3\text{C}_2\text{T}_x$ (-1.57 eV) relative to pure Cu (-1.85 eV) enhances NO_3^- adsorption, while the rate-determining step shifts from the initial NO_3^- adsorption on monometallic

surfaces to the final NH_3 desorption on the bimetallic catalyst, collectively accounting for the outstanding nitrate reduction to ammonia selectivity and durability over nine consecutive cycles.

5.5. Heterostructured MXene catalysts

Technically, the surface of MXene nanolayers possesses a high surface area and strong interlayer attraction, which can affect the electrochemical properties of pure MXenes.^[121] As a result, the practical performance of pure MXene remains significantly lower than its expected capacity. To address these limitations, numerous studies^[122–125] have employed MXene as a conductive substrate and integrated it with metal oxides to construct highly efficient heterostructures. These developed composites leverage synergistic effects among the constituent components, leading to substantially enhanced electrocatalytic performance in recent years.^[121] In this context, Phu *et al.*^[16] constructed heterogeneous 2D/2D $\text{MnO}_2/\text{MXene}$ hybrids by vertically growing $\delta\text{-MnO}_2$ nanoflakes onto few-layer $\text{Ti}_3\text{C}_2\text{T}_x$ MXene nanosheets via a KMnO_4 redox-driven precipitation route, exploiting the reducing capability of MXene's surface functional groups to trigger in-situ MnO_2 nucleation while simultaneously preserving the 2D layered MXene architecture. The KMnO_4 precursor concentration served as the decisive morphological lever, yielding sparse, dense, and urchin-type $\text{MnO}_2/\text{MXene}$ configurations at 0.001, 0.005, and 0.01 mol L^{-1} respectively (**Fig. 12a**), with the dense variant identified as optimal because excessive MnO_2 loading at 0.01 mol L^{-1} generated congestive urchin-like agglomerates that blocked mass transport channels (**Fig. 12b**). HR-TEM confirmed MnO_2 (002) lattice fringes at 0.35 nm decorating the MXene skeleton (**Figs. 12c and d**), while the selected area electron diffraction (SAED) patterns resolved three concentric diffraction rings assignable to MnO_2 (002), MXene (102), and MXene (110) planes (**Fig. 12e**), collectively verifying that both phases retained crystallinity in the composite. Crucially, strong interfacial electronic coupling between the two components was established through convergent spectroscopic evidence: Raman spectroscopy showed a progressive blueshift of the Mn–O symmetric stretching (E_g mode, 600–650 cm^{-1}) with increasing MnO_2 loading (**Fig. 12f**), while XPS Mn 2p analysis revealed a positive shift of the Mn^{3+} $2p_{3/2}$ binding energy upon MXene integration, and Ti 2p spectra showed a concurrent decrease in Ti^{4+} intensity and a redshift in Ti^{4+} binding energy, together indicating electron transfer from Mn^{3+} sites in MnO_2 to

Ti^{4+} sites in MXene that strengthens Mn–O bonds and improves overall conductivity. The electrochemical consequences of this 2D/2D interfacial engineering were unambiguous: dense $\text{MnO}_2/\text{MXene}$ achieved a current density of 91.6 mA cm^{-2} at -1.0 V vs. RHE, the lowest Tafel slope among all samples (0.353 mV dec^{-1} vs. 0.878 mV dec^{-1} for pure MnO_2), the lowest charge transfer resistance ($R_{\text{CT}} = 5.001 \Omega$), and the highest C_{dl} of 4.49 mF cm^{-2} , 7.7 times that of pure MnO_2 (0.581 mF cm^{-2}), reflecting the largest electrochemically active surface area (**Fig. 12g**). These properties translated into peak NH_3 production metrics of $14.06 \pm 0.48 \text{ mg h}^{-1} \text{ mg}_{\text{cat}}^{-1}$ at -1.2 V vs. RHE and maximum FE_{NH_3} of $85.23 \pm 1.62\%$ at -1.0 V vs. RHE (**Figs. 12h and i**), with FE_{NH_3} maintained above 75% across six consecutive cycles and FE_{NH_3} reaching 88.2% at pH 10, confirming that alkaline conditions favor H_{ads} generation critical to the hydrogenation steps of eNO_3^- RR. Time-resolved concentration tracking over 8 h showed linear NO_3^- depletion accompanied by NH_3 accumulation and persistently low NO_2^- levels (**Fig. 12j**), with pseudo-first-order kinetic modeling yielding a rate constant of 0.291 h^{-1} . Extending functionality beyond conventional electrolysis, a Zn– NO_3^- battery (**Fig. 12k**) incorporating dense $\text{MnO}_2/\text{MXene}$ as cathode and a polished Zn plate recovered from spent Zn-carbon batteries as anode delivered a peak power density of 0.323 mW cm^{-2} (**Fig. 12l**), a stable open-circuit potential of 1.04 V over 10 h (**Fig. 12m**), and FE_{NH_3} of $79.63 \pm 4.51\%$ at 2.5 mA cm^{-2} . During discharge, Zn dissolution drove the electrochemical reduction of NO_3^- to NH_3 , with the electrode reactions described as follows:



Overall reaction

To benchmark the performance of this work compared with prior studies, a comparative chart was constructed based on catalytic activity and Faradaic efficiency in a neutral electrolyte (**Fig. 12n**), demonstrating the simultaneous triad of waste Zn recycling, electricity generation, and value-added ammonia production from nitrate-contaminated streams.

On the other hand, a variety of transition-metal-based catalysts have been developed for robust MXene-based heterostructures toward eNO_3^- RR due to their unique electronic structure.^[126] Among them, Co-based catalysts have attracted particular attention due to their cost-effectiveness, high nitrate-ion adsorption, and

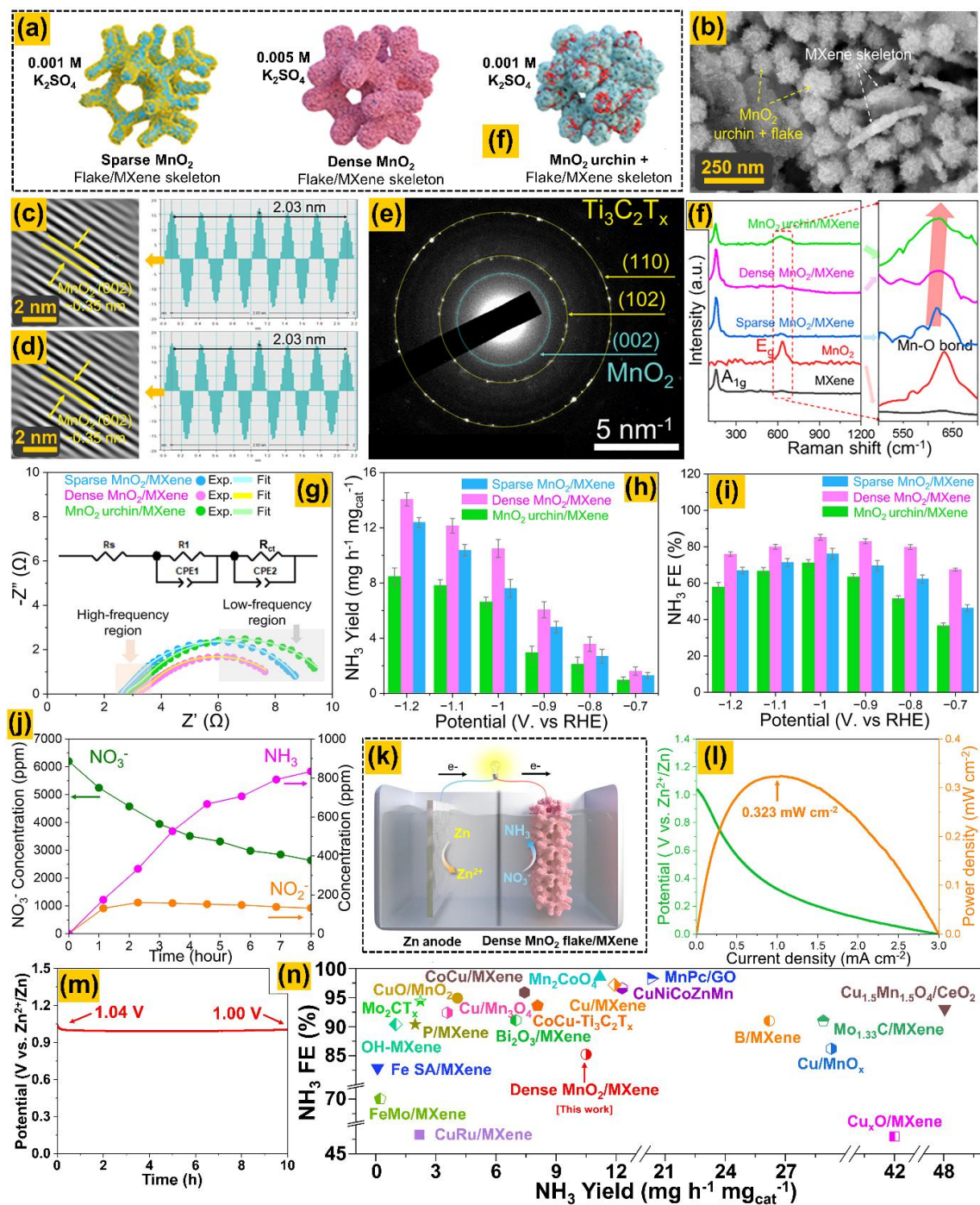


Figure 12. (a) Schematic illustration of as-prepared MnO₂/MXene catalysts. (b) FE-SEM micrographs of as-prepared MnO₂ urchin/MXene (scale bar, 250 nm); (c and d) corresponding lattice spacings (scale bar, 2 nm); and (e) the SAED pattern (scale bar, 5 nm⁻¹). (f) XRD patterns of the as-prepared MXene, MnO₂, and MnO₂/MXene catalysts. (g) Electrochemical impedance spectroscopy with an alternating current amplitude of 5 mV at an applied potential of -0.6 V vs. RHE. (h) Faradaic efficiency and (i) yield rate of NH₃ as a function of overpotential for different catalysts (Error bars represent the standard deviation in yield rate and FE calculated after three tests for repeatability). (j) Concentration-time curves of the NO₃⁻, NO₂⁻, and NH₃ in eNO₃ RR for 8 h. (k) Schematic diagram, (l) polarization discharge curves and power density, and (m) open-circuit potential of the dense MnO₂/MXene-based Zn-NO₃⁻ battery. (n) Performance comparison of different reported Mn-based and MXene-based catalysts for eNO₃⁻ RR to NH₃ production in neutral electrolyte.^[16] (Copyright 2025, Elsevier)

favorable contribution to hydrogen adsorption during this process.^[120, 127] However, their further application is hindered by slow reaction kinetics, low product selectivity, and insufficient stability.^[128] According to the literature, the nitrate anion exhibits Lewis base characteristics, while boron (B) possesses an unoccupied 2p orbital that enables it to act as a Lewis acid by accepting electron pairs. In line with Lewis acid-base interaction theory, the strategic incorporation of boron is therefore expected to strengthen NO₃[−] adsorption through favorable acid-base pairing, thereby enhancing the selectivity and efficiency of Co-based catalysts toward NO₃RR while suppressing the parasitic HER.^[127, 129–131] In this regard, Yu *et al.*^[127] conceived a Co₂B@MXene heterostructure featuring a spontaneously built-in electric field (BIEF) by sequentially applying molten salt etching and in-situ borothermal reduction strategies (**Fig. 13a**), where the work function mismatch between Ti₃C₂T_x MXene (4.092 eV) and Co₂B (5.137 eV), as shown in (**Fig. 13b**), drove spontaneous electron migration from MXene toward Co₂B until Fermi level equilibration (**Fig. 13c**), a phenomenon visually captured through charge density difference mapping in **Fig. 10d** and experimentally validated by UPS measurements. Structural integrity of the resulting heterointerface was confirmed by HR-TEM imaging (**Fig. 13e**), which resolved Co₂B (200) and Ti₃C₂T_x (002) lattice fringes of 0.263 and 1.119 nm respectively at a clearly demarcated phase boundary, while XPS analysis (**Fig. 13f**) revealed upward binding energy shifts for Ti–C, Ti²⁺, and Ti³⁺ species in Co₂B@MXene relative to Co@MXene, providing direct spectroscopic evidence of interfacial charge redistribution driven by built-in electric field (BIEF). Electrochemically, Co₂B@MXene outperformed Co@MXene across all tested potentials, delivering a peak NH₃ yield rate of 7.34 mg h^{−1} mg_{cat}^{−1} and FE of 92.13% at −0.7 V vs. RHE, alongside a higher C_d (0.86 mF cm^{−2}) and ECSA (21.38 cm², **Fig. 13g**), reflecting the enlarged active surface area and accelerated reaction kinetics conferred by the heterostructure. Extending beyond conventional electrolysis, the assembled Zn–NO₃[−] battery incorporating Co₂B@MXene achieved an open circuit voltage of 1.38 V (**Fig. 13h**), a peak power density of 6.86 mW cm^{−2}, and an FE_{NH₃} of 91.74% at 6 mA cm^{−2} (**Fig. 13i**), demonstrating the simultaneous triad of nitrate removal, ammonia synthesis, and energy output. Mechanistic interrogation through hydrogen gas detection, tert-butanol quenching, potassium thiocyanate (KSCN) poisoning, EPR spin-trapping, and in-situ FTIR unambiguously delineated a tandem catalytic pathway in which B sites, owing to their

Lewis acid character, preferentially adsorb and activate NO₃[−] (adsorption energy: −3.14 eV vs. −1.49 eV at Co), driving the initial deoxygenation sequence NO₃[−] → *NO₂, while Co sites catalyze H₂O dissociation to supply abundant H_{ads} for the subsequent hydrogenation cascade (*NO₂ → *NH₃) (**Figs. 13j** and **k**), with PDOS analysis confirming stronger orbital overlap between B-p and *NO₃-p states compared to Co-d, thus providing a theoretical foundation for the superior activity and remarkable 65 h chronoamperometric stability of the Co₂B@MXene catalyst.

5.6. Single-atom-anchored MXene

Since Zhang *et al.*^[132] first proposed the concept of single-atom catalysts (SACs) in 2011, SACs have become one of the most dynamic frontier fields in catalysis, including CO oxidation, hydrogen evolution reaction, oxygen reduction reaction (ORR), oxygen evolution reaction (OER), CO₂ reduction reaction (CO₂RR), NRR, and NO₃[−]RR, primarily due to their low cost and near-maximum atom utilization efficiency.^[133, 134] Notably, in comparison to traditional catalysts, SACs provide nearly total utilization of metal atoms, enabling high catalytic activity to be achieved even with low metal loadings, thus reducing overall production expenses.^[135] Due to the uniformity and homogeneity of active sites, SACs allow for precise adjustment of their coordination structure, demonstrating high efficiency for targeted reactions and product selectivity.^[135, 136] While SACs have considerable potential, they also pose significant technical challenges. Specifically, the limitation to one active site poses difficulties for SACs in addressing linear scaling relationships between reaction intermediates in intricate reactions.^[59, 137] In this case, obtaining stable, well-dispersed SACs typically necessitates fixing isolated metal atoms onto an appropriate substrate. In this configuration, significant charge transfer occurs via the attachment of metal atoms to reactive areas on the support. Typical substrates used for the immobilization of these metal atoms consist of metal oxides, metal-organic frameworks (MOFs), molybdenum disulfide (MoS₂), graphene, and similar materials.^[135]

Of them, stabilizing SACs on MXene supports has emerged as a particularly promising strategy to further enhance their electrocatalytic performance. For example, Gao *et al.*^[138] conducted a comprehensive DFT-based computational screening of 22 transition metal SACs embedded on oxygen vacancy-engineered Ti₃C₂O₂ MXene (TM/O_v-MXene), motivated by the observation that the pristine MXene basal plane, fully

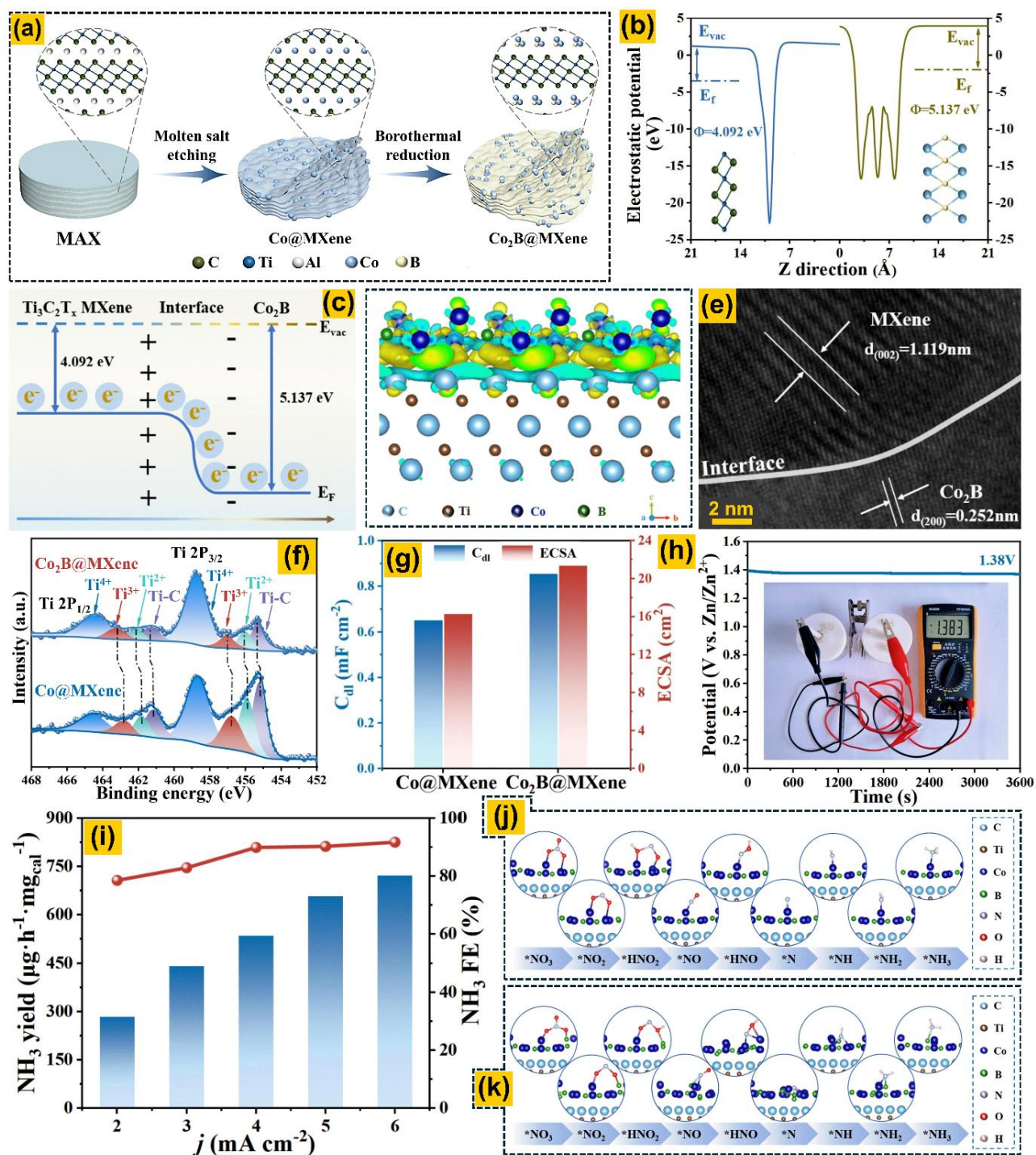


Figure 13. (a) The preparation process of $\text{Co}_2\text{B}@MXene$ heterostructure. (b) The work functions of $\text{Ti}_3\text{C}_2\text{Tx}$ MXene and Co_2B . (c) Electron movement between $\text{Ti}_3\text{C}_2\text{Tx}$ MXene and Co_2B . (d) The differential charge density of the $\text{Co}_2\text{B}@MXene$ heterostructure (yellow and blue regions represent increases and decreases in charge density). (e) HR-TEM image of $\text{Co}_2\text{B}@MXene$. (f) Ti 2p XPS spectra of $\text{Co}@MXene$ and $\text{Co}_2\text{B}@MXene$ catalysts. (g) Comparison of C_{dl} and ECSA of $\text{Co}@MXene$ and $\text{Co}_2\text{B}@MXene$. (h) Open-circuit voltage of $\text{Co}_2\text{B}@MXene$ -based $\text{Zn}-\text{NO}_3^-$ battery. (i) FE and NH_3 yield rate of $\text{Zn}-\text{NO}_3^-$ battery with $\text{Co}_2\text{B}@MXene$ catalyst cathode. Models of adsorption-desorption intermediates at (j) Co and (k) B sites in $\text{Co}_2\text{B}@MXene$.^[127] (Copyright 2025, Elsevier)

functionalized, lacks accessible metal coordination sites for PCET reactions, making vacancy engineering an indispensable prerequisite for catalytic activity. The structural model was constructed by first removing one surface O atom from $\text{Ti}_3\text{C}_2\text{O}_2$ to create an oxygen vacancy, followed by substituting the exposed Ti site with different TM atoms (**Fig. 14a**), with the resulting NO_3^- adsorption energy ($\Delta G^*\text{NO}_3$) identified, through a linear scaling relationship with $R^2 = 0.854$ and 0.968 , as the primary activity descriptor for NO_3RR limiting potential across the entire TM series (**Fig. 14b**). A critical initial screening criterion was established by comparing ΔG_{NO_3} against $\Delta G^*\text{H}$ across all 22 TM/ O_v -MXenes (**Fig. 14c**): 14 candidates including Cr, Mn, Fe, Ni, Cu, Ag, and Au exhibited more negative NO_3^- adsorption than proton adsorption, confirming intrinsic preference for eNO_3RR over HER, while Ta, W, and Re were eliminated because adsorbed NO_3^- spontaneously decomposed and filled the vacancy with an O atom, blocking further reduction. Among the surviving candidates, a periodic trend emerged in which limiting potentials became progressively less negative moving from left to right across the d-block (groups 3 through 12 of the periodic table), and a contour plot constructed as a function of the two potential-determining steps, $^*\text{NO}_3 + \text{H}^+ + \text{e}^- \rightarrow ^*\text{HNO}_3$ and $^*\text{NO}_2 + \text{H}^+ + \text{e}^- \rightarrow ^*\text{HNO}_2$ (**Fig. 14d**), identified Ag, Cu, Pt, Pd, Ni, and Au as residing in the low-limiting-potential red zone, with Ag/ O_v -MXene and Cu/ O_v -MXene singled out as the optimal precious-metal and non-precious-metal candidates respectively, carrying limiting potentials of only -0.24 and -0.34 V. Detailed free energy diagrams for both catalysts via the preferred 1-O binding pathway (**Figs. 14e and f**) traced the full reaction coordinate from $^*\text{NO}_3$ through $^*\text{NO}_3\text{H}$, $^*\text{NO}_2$, $^*\text{NO}_2\text{H}$, $^*\text{NO}$, $^*\text{NOH}$, $^*\text{N}$, $^*\text{NH}$, $^*\text{NH}_2$, $^*\text{NH}_3$ to desorbed NH_3 , with the rate-limiting $^*\text{NO}_2 + \text{H}^+ + \text{e}^- \rightarrow ^*\text{NO}_2\text{H}$ step requiring only 0.24 and 0.34 eV on Ag and Cu respectively, while competing byproduct release pathways faced substantially higher barriers, up to 1.43 eV (NO_2), 0.91 eV (NO), 0.76 eV (N_2O), and 0.95 eV (N_2) on Ag/ O_v -MXene, and 1.65 , 1.03 , 0.97 , and 0.75 eV on Cu/ O_v -MXene, collectively rationalizing the exceptional NH_3 selectivity of both catalysts. The electronic origins of this selectivity were traced through PDOS and charge density difference analysis: d-orbital hybridization between Ag or Cu and the $2p$ orbital of NO_3^- upon adsorption transferred 0.74 and 0.75 e^- respectively from the TM SAC to NO_3^- , while d-band center analysis revealed that Ag (-3.34 eV) and Cu (-2.62 eV) occupy the moderate d-band center range that avoids the extremes of too-strong (Cr, -0.74 eV) or too-weak (Au, -4.70 eV) NO_3^- binding.

For the NO_3RR mechanism, two possible binding configurations of $^*\text{NO}_2$, denoted as the 1-O and 2-O modes, were considered on the TM/ O_v -MXene surfaces and the corresponding intermediate structures for the 1-O and 2-O pathways are presented in **Fig. 14g**. Since the adsorption energy of $^*\text{NO}_2$ in the 1-O configuration is consistently lower than that of the 2-O configuration on both Ag/ O_v -MXene and Cu/ O_v -MXene, the 1-O pathway is expected to dominate, despite the 2-O pathway exhibiting a lower limiting potential. The thermodynamic and kinetic stability of both catalysts was validated through calculated formation energies ($E_{\text{form}} = +2.30$ eV for Ag, $+2.41$ eV for Cu, both lower than the experimentally realized $+2.62$ eV for Pt-doped $\text{Mo}_2\text{TiC}_2\text{O}_2$) and 10 ps by the ab initio molecular dynamics (AIMD) simulations at 500 K both in vacuum and in explicit H_2O solvent (**Figs. 14h and i**), confirming structural integrity throughout, and establishing Ag/ O_v -MXene and Cu/ O_v -MXene as computationally validated, high-activity, high-selectivity, and thermodynamically stable SAC platforms for ambient electrochemical NO_3^- -to- NH_3 conversion.

5.7. MXene/organic-inorganic-based catalyst

From a technical standpoint, one inherent challenge of MXenes is their high susceptibility to oxidation, which significantly impairs electrochemical performance and restricts ion/electrolyte transport. To address this limitation, a promising strategy involves the rational design of hybrid composite systems that integrate MXene with organic and inorganic materials.^[139, 140] In this manner, Zhou *et al.*^[21] developed novel 2D hybrid materials, $\text{NMo}_6\text{-Tris@MXC}$ ($\text{N} = \text{Fe}, \text{Co}, \text{Ni}$), by covalently grafting tris(hydroxymethyl)methane-functionalized Anderson-type polyoxometalates ($\text{NMo}_6\text{-Tris}$) onto carboxylated $\text{Ti}_3\text{C}_2\text{T}_x$ MXene nanosheets via amide linkages using a “functionalize-then-condense” strategy for electrochemical nitrate reduction to ammonia. The successful synthesis was confirmed through complementary characterization techniques, where TEM analyses (**Fig. 15a**) revealed a distinctive pleated nanosheet morphology with uniformly distributed polyoxometalate (POM) nanoclusters, the atomic force microscope (AFM) measurements (**Figs. 15b and c**) demonstrated a thickness increase from 0.212 μm for pristine MXene to 1.37 μm for $\text{CoMo}_6\text{-Tris@MXC}$, and FTIR (**Fig. 15d**) and Raman (**Fig. 15e**) analyses collectively confirmed the formation of covalent amide linkages between components. XPS characterization revealed significant binding energy shifts at the $\text{NMo}_6\text{-}$

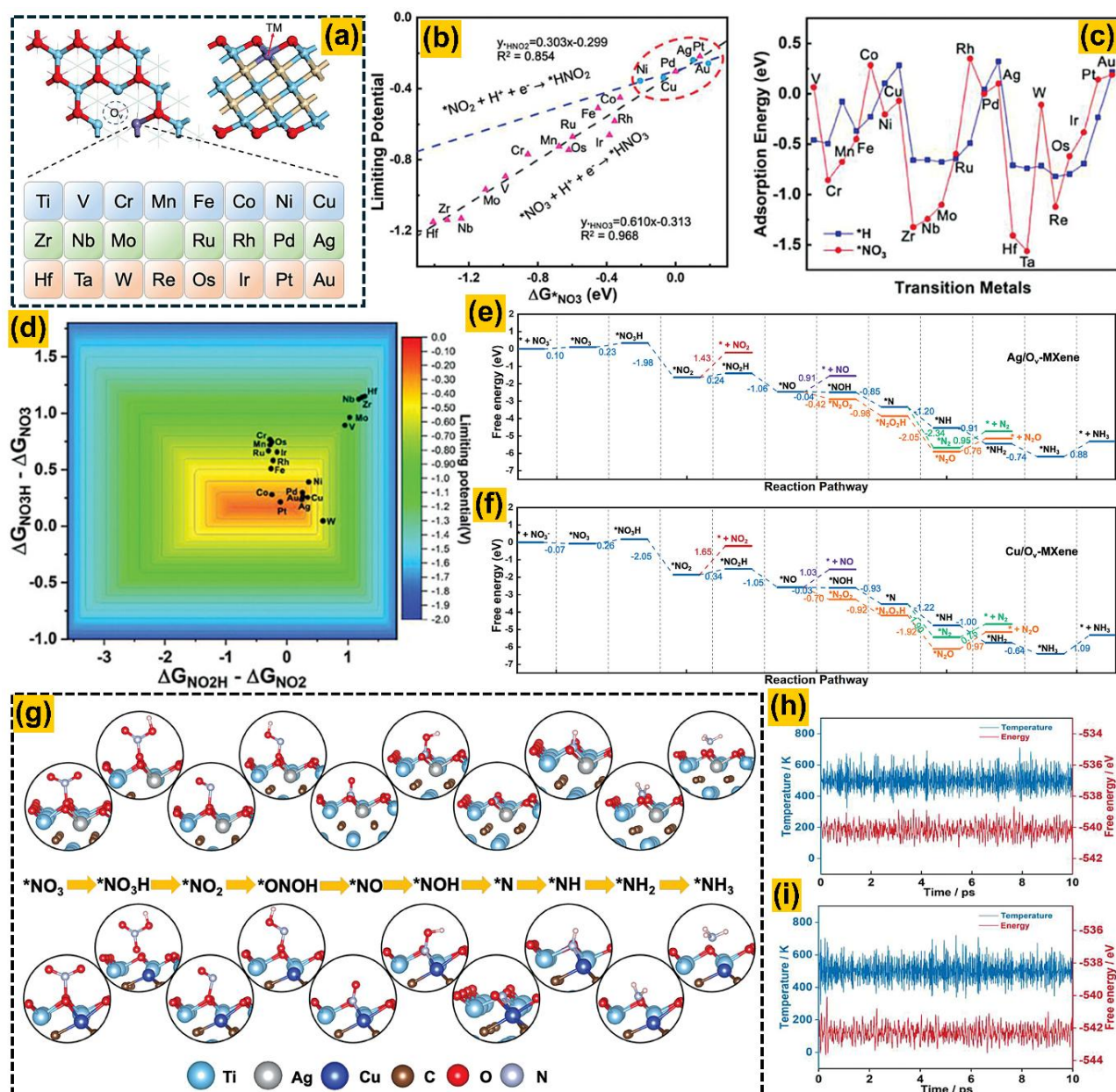


Figure 14. (a) Top and side views of the atomic structure of TM/O_v-MXene. (Atom labels: C (white), Ti (blue), O (red), and TM (purple).) (b) Summary of limiting potentials on TM/O_v-MXene for NO₃RR. (c) Comparison of adsorption energies of NO₃[−] and H⁺ on TM/O_v-MXene. (d) Contour plot of limiting potential as a function of two potential-determining steps ($\text{*NO}_3 + \text{H}^+ + \text{e}^- \rightarrow \text{*HNO}_3$ and $\text{*NO}_2 + \text{H}^+ + \text{e}^- \rightarrow \text{*HNO}_2$). (e, f) Free-energy diagrams ($U = 0$ V) for eNO₃RR on Ag/O_v-MXene and Cu/O_v-MXene, respectively. The pathways to the release of NO₂, NO, N₂, and N₂O are also plotted for comparison. (g) Corresponding structures of eNO₃RR intermediates adsorbed on Ag/O_v-MXene (above) and Cu/O_v-MXene (below), respectively. (h, i) Energy and temperature evolution versus the AIMD time for Ag/O_v-MXene and Cu/O_v-MXene.^[138] (Copyright 2023, Wiley)

MXC interface, including a 1.8 eV shift in Co 2p (Fig. 15f) and a 0.6 eV shift in Mo 3d (Fig. 15g), indicating substantial interfacial electron redistribution that optimizes surface electronic states. Among the synthesized composites, CoMo₆-Tris@MXC exhibited

the highest NO₃RR performance, achieving an NH₃ yield of 4.993 mg h^{−1} mg_{cat}^{−1} and a Faradaic efficiency of 98.7% at −1.0 V vs. RHE, significantly surpassing pristine MXene (47.5% FE) and parent POMs, while maintaining over 95% activity retention after 12 h of

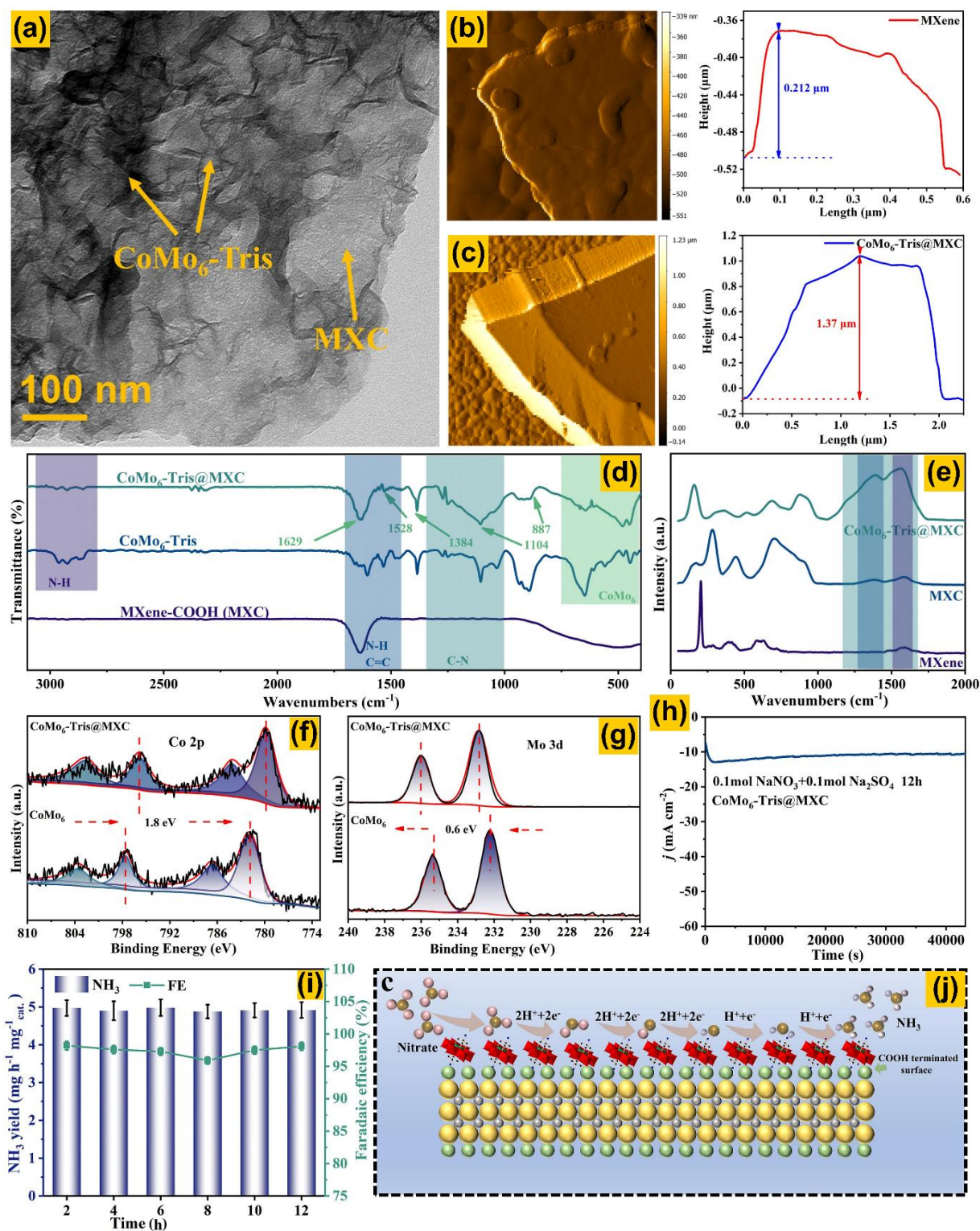


Figure 15. (a) TEM image of epitaxial growth of CoMo₆-Tris on MXC. AFM images and corresponding height profiles of (b) pure MXene and (c) CoMo₆-Tris@MXC. (d) FTIR and (e) Raman spectrums of CoMo₆-Tris@MXC, MXC, and MXene. The narrow XPS spectra of CoMo₆-Tris@MXC and MXene: (f) Co 2p and (g) Mo 3d. (h) j-t curve working continuously for 12 h. (i) FE and NH₃ yield for each 2 h period during the 12 h reaction. (j) The proposed reaction path in the catalytic process.^[21] (Copyright 2025, Elsevier)

continuous operation with negligible structural degradation (Figs. 15h and i). Isotopic labeling experiments using $^{14}\text{N}/^{15}\text{N}$ -enriched nitrate, with ^1H NMR analysis, unequivocally confirmed that nitrate was the exclusive nitrogen source. In-situ FTIR spectroscopy elucidated the reaction pathway as $\text{NO}_3^- \rightarrow * \text{NO}_2 \rightarrow * \text{NO} \rightarrow * \text{NH} \rightarrow * \text{NH}_2 \rightarrow \text{NH}_4^+$ (Fig. 15j), demonstrating that the covalent NMo_6 integration suppresses undesirable NO_2^- byproduct formation by 23.99% compared to pristine MXene, thereby enhancing ammonia selectivity through synergistic electronic and structural effects between the conductive MXene framework and the redox-active POM clusters.

5.8. Predicting NH_3 synthesis of MXene-based catalyst by machine learning

From a technical perspective, a comprehensive understanding of the mechanisms underlying electrocatalytic NH_3 synthesis is essential for the rapid identification and development of high-performance catalysts. Such mechanistic insight can be effectively achieved by synergistically combining advanced in-situ/operando characterization techniques with rigorous theoretical calculations.^[5] Beyond experimental approaches, the integration of data-driven computational methods has further accelerated progress in this field, offering powerful complementary tools for catalyst discovery and optimization. The intersection of statistical methods and machine learning (ML) techniques with natural sciences has proven highly fruitful across a broad spectrum of problems. For instance, in chemistry and catalysis, such approaches have enabled effective classification of large molecular databases, rapid screening of catalysts using predictive models trained on extensive datasets, and the solution of inverse problems to identify systems with a desired target response.^[141] These capabilities have naturally extended to electrocatalysis, where the complexity of reaction pathways and the vast compositional space of candidate materials make data-driven strategies particularly valuable. ML, as a transformative subset of artificial intelligence, has emerged as a powerful tool in catalysis research. By harnessing data-driven prediction and optimization, ML enables the rapid identification of key activity descriptors and the systematic enhancement of catalytic performance. Recent advances have particularly highlighted the effectiveness of MXene-based catalysts in the nitrate reduction reaction, where sophisticated feature engineering strategies have led to substantial improvements in catalyst design and activity optimization,^[142] establishing ML as an indispensable

component of modern electrocatalyst development.

It is important to highlight that, even though data-driven methods have significant potential for speeding up catalyst discovery, research explicitly integrating machine learning with MXene-based electrocatalysts for NO_3^- reduction is still limited. Accordingly, Jia *et al.*^[142] conducted a dual-strategy computational investigation combining first-principles DFT calculations with six machine learning algorithms to systematically screen 13 single transition metal atoms (Sc, Ti, V, Cr, Cu, Zr, Nb, Mo, Tc, Ru, Hf, Ta, and W) anchored on oxygen vacancy-engineered M_2CO_2 MXenes ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$), motivated by the observation that pristine bare MXenes exhibit strongly unfavorable NO_3^- adsorption energies of +2.30, +2.25, and +2.16 eV for Cr_2CO_2 , Mo_2CO_2 , and W_2CO_2 respectively, which oxygen vacancy introduction dramatically reversed to -0.93, -0.90, and -1.56 eV, yet with still-unsatisfactory limiting potentials around -1.0 V demanding further optimization through TM doping. Among all 39 $\text{TM@O}_v\text{-M}_2\text{CO}_2$ configurations evaluated, $\text{Cu@O}_v\text{-Cr}_2\text{CO}_2$, $\text{Ru@O}_v\text{-Mo}_2\text{CO}_2$, $\text{Hf@O}_v\text{-Mo}_2\text{CO}_2$, and $\text{Tc@O}_v\text{-W}_2\text{CO}_2$ emerged as optimal catalysts with limiting potentials of -0.36, -0.37, -0.37, and -0.42 V, respectively (Fig. 16a), all exhibiting more negative $\Delta G(*\text{NO}_3)$ than $\Delta G(*\text{H})$ across the entire TM series, confirming intrinsic NO_3RR preference over competing HER. As can be seen in Fig. 16b, for $\text{TM@O}_v\text{-Cr}_2\text{CO}_2$ and $\text{TM@O}_v\text{-Mo}_2\text{CO}_2$, the PDS is $*\text{NO}_2\text{H}$ generated from $*\text{NO}_2$ ($*\text{NO}_2 + \text{H}^+ + e^- \rightarrow *\text{NO}_2\text{H}$) except Cu doped and Hf doped. Electronic structure analysis through PDOS, COHP (crystal orbital Hamiltonian population), and charge density difference calculations (Figs. 16c and d) revealed that d-p orbital hybridization between TM d-orbitals and $*\text{NO}_3$ p-orbitals in the -5 to -30 eV energy range drives effective electron transfer, with Hf and Tc donating substantially more electrons to adsorbed NO_3^- (0.93 and 0.95 e respectively) than Cu and Ru (0.53 and 0.58 e), explaining their stronger initial nitrate binding while maintaining a consistent “donor-acceptor” charge transfer pattern throughout the full reduction sequence wherein the $\text{O}_v\text{-M}_2\text{CO}_2$ substrate (moiety1) serves as electron reservoir, the TM active site (moiety2) maintains persistent positive charge, and adsorbed intermediates (moiety3) accumulate electrons (Figs. 16e and f). The machine learning component, the central focus of this study, employed six regression algorithms (GBR (Gradient Boosting Regression), KRR (Kernel Ridge Regression), XGBR (Extreme Gradient Boosting Regression), RFR (Random Forest Regression), ENR (Elastic Net Regression), and SVR (Support Vector Regression)) trained on 14 intrinsic

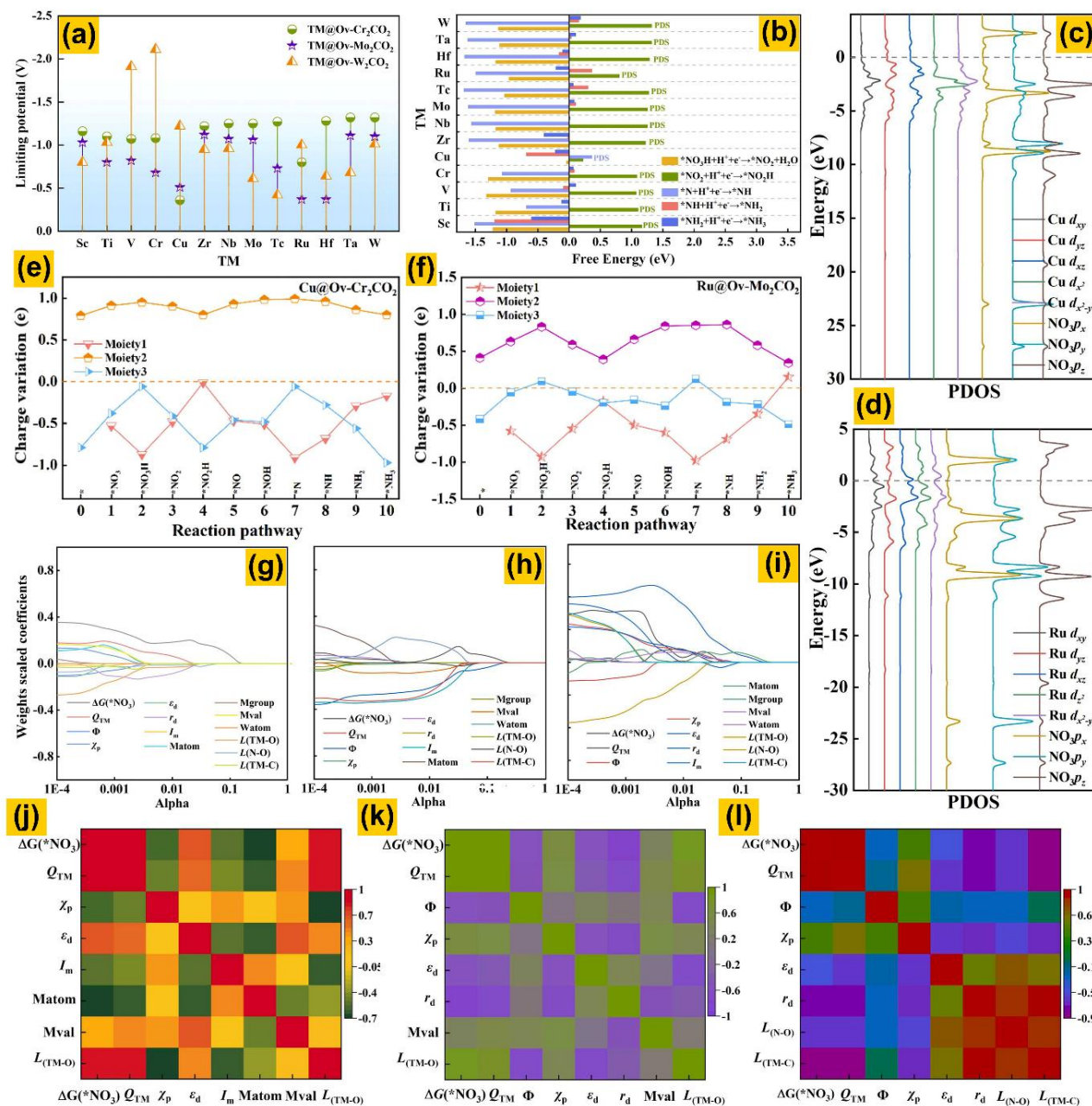


Figure 16. (a) The limiting potentials for NO₃RR on TM@O_v-Cr₂CO₂, TM@O_v-Mo₂CO₂, and TM@O_v-W₂CO₂. (b) The potential-determining step of NO₃RR on TM@O_v-Cr₂CO₂. Crystal orbital Hamiltonian population of NO₃⁻ absorbed on (c) Cu@O_v-Cr₂CO₂ and (d) Ru@O_v-Mo₂CO₂, respectively. Charge-transfer distribution during each protonation step of NO₃⁻RR among the O_v-M₂CO₂ substrate (moiety 1), TM (moiety 2), and absorbed molecules (moiety 3) on (e) Cu@O_v-Cr₂CO₂ and (f) Ru@O_v-Mo₂CO₂, respectively. The feature selection with LASSO analyzes the relationship between the LASSO regression coefficients and the alpha parameter of (g) TM@O_v-Cr₂CO₂, (h) TM@O_v-Mo₂CO₂, and (i) TM@O_v-W₂CO₂. The plot of Pearson correlation coefficient of the selected feature importance of (j) TM@O_v-Cr₂CO₂, (k) TM@O_v-Mo₂CO₂, and (l) TM@O_v-W₂CO₂.^[142] (Copyright 2026, Elsevier)

descriptors encoding electronic, geometric, and atomic properties of each TM@O_v-M₂CO₂ catalyst, with performance metrics evaluated by R^2 and RMSE (root-mean squared error). Across all three MXene families,

GBR consistently achieved the highest predictive accuracy with $R^2 = 0.998/0.999/0.999$ and RMSE = 0.001/0.001/0.001 for TM@O_v-Cr₂CO₂, TM@O_v-Mo₂CO₂, and TM@O_v-W₂CO₂, respectively,

substantially outperforming SVR (R^2 as low as 0.492 for Mo_2CO_2) and confirming GBR as the optimal predictive model. The least solution shrinkage and selection operator (LASSO)-based feature selection (Figs. 16g-i) reduced the 14-descriptor space to 8 most informative features per MXene family, after which GBR feature importance analysis identified the two dominant descriptors: for $\text{TM@O}_v\text{-Cr}_2\text{CO}_2$, charge transfer of TM (Q_{TM}) ranked first at 45.77% importance followed by $\Delta G(*\text{NO}_3)$ at 33.19%; for $\text{TM@O}_v\text{-Mo}_2\text{CO}_2$, $\Delta G(*\text{NO}_3)$ ranked first at 34.15% and Q_{TM} second at 32.95%; while for $\text{TM@O}_v\text{-W}_2\text{CO}_2$ a shift emerged with the metallic radius of TM (r_d)

dominating at 70.95% and $\Delta G(*\text{NO}_3)$ second at 7.15%, a substrate-dependent descriptor divergence that Pearson correlation matrices (Figs. 16j-l) confirmed through strong $\Delta G(*\text{NO}_3)\text{-}Q_{\text{TM}}$ coupling for Cr and Mo systems versus $\Delta G(*\text{NO}_3)\text{-}r_d$ coupling for W systems, collectively establishing that machine learning not only validated DFT-derived activity trends but crucially revealed substrate-specific electronic and structural descriptors governing $\text{eNO}_3\text{-RR}$ performance that simple electronic structure analysis alone could not disentangle.

Table 1 present a comparison of MXene-based catalysts for NH_3 synthesis via $\text{eNO}_3\text{-RR}$.^[79, 143]

Table 1. Comparison of MXene-based catalysts for NH_3 synthesis via $\text{eNO}_3\text{-RR}$.

Electrocatalysts	Electrolytes	Potential	FE	NH_3 yield	Ref.
Of-TiMX	0.5M K_2SO_4 + 200 mg L^{-1} KNO_3	-1.7 V vs. SCE	90.4%	0.99 $\text{mg h}^{-1} \text{cm}^{-2}$	[105]
CuPc@MXene	0.5M Na_2SO_4 + 50 mg L^{-1} NaNO_3	-1.06 V vs. RHE	94%	2.72 $\text{mg h}^{-1} \text{cm}^{-2}$	[144]
$\text{Co}_2\text{B@MXene}$	0.1 M K_2SO_4 + 0.1 M KNO_3	-0.7 V vs. RHE	92.13%	7.34 $\text{mg h}^{-1} \text{mg}_{\text{cat}}^{-1}$	[127]
$\text{CoCu-Ti}_3\text{C}_2\text{T}_x$	0.1 M K_2SO_4 + 0.1 M KNO_3	-0.7 V vs. RHE	93.6%	8.08 $\text{mg h}^{-1} \text{mg}_{\text{cat}}^{-1}$	[145]
$\text{Co}_7\text{Cu}_3\text{@PM}$	0.1 M K_2SO_4 + 0.1 M KNO_3	-0.7 V vs. RHE	95.9%	7.43 $\text{mg h}^{-1} \text{mg}_{\text{cat}}^{-1}$	[146]
11% $\text{Bi}_2\text{O}_3\text{/MXene}$	0.5 M Na_2SO_4 + 1000 mg L^{-1} KNO_3	-1.8 V vs. SCE	91.1%	$\sim 7.00 \text{ mg h}^{-1} \text{cm}^{-2}$	[147]
$\text{Fe}_1\text{Cu}_2\text{@MXene}$	0.5 M Na_2SO_4 + 100 mg L^{-1} KNO_3	-0.95 V vs. RHE	95.6%	90 mg after 8 h	[148]
$\text{Mo}_2\text{CT}_x\text{:Fe}$	0.5 M Na_2SO_4 + 100 mM NaNO_3	-0.6 V vs. RHE	70%	12.9 $\mu\text{mol h}^{-1} \text{mg}_{\text{cat}}^{-1}$	[119]
FeSA/MXene	0.1 M Na_2SO_4 + 50 mg L^{-1} NaNO_3	-1.4 V vs. Ag/AgCl	82.9%	$\sim 90 \mu\text{g h}^{-1} \text{cm}^{-2}$	[149]

6. Techno-economic analysis of $\text{eNO}_3\text{-RR}$

Contaminant loads in wastewater, nitrogen, phosphorus, and potassium, carry an estimated annual value of \$100 billion, with almost 80% remaining untreated.^[19] A recent techno-economic evaluation of electrochemical nitrate-to-ammonia, a reaction notably simpler than N_2 reduction, found that both capital and operating expenses remain considerably higher than the market price of the produced fertilizer unless significant policy incentives or environmental credits are included.^[150] However, the full economic viability of $\text{NO}_3\text{-RR}$ still needs improvement through technological progress and scaling, it remains promising.^[151]

To attain sustainable $\text{eNO}_3\text{-RR}$ for NH_3 synthesis, it is essential to combine life cycle assessment (LCA) with techno-economic analysis (TEA). LCA is essential for identifying and reducing environmental impacts across the full life cycle to minimize resource consumption and emissions. TEA assesses the economic viability of $\text{eNO}_3\text{-RR}$ processes by examining anticipated income, energy efficiency, and both capital and operational expenses. By combining LCA and TEA findings, decision-makers can identify ammonia generation approaches that are both

environmentally friendly and economically feasible. This comprehensive approach ensures a balanced evaluation of ecological and economic aspects, leading to more informed sustainable decisions about the creation and use of novel electrocatalysts in $\text{eNO}_3\text{-RR}$.^[152] Most reported catalysts currently achieve current densities below these benchmarks. For instance, engineered electrocatalysts with dual atoms and defects could elevate FE to 50%-60%, yet they still produce only tens of $\mu\text{g h}^{-1} \text{mg}^{-1}$ in standard tests, indicating that their active-site densities result in significantly lower NH_3 output than TEA objectives.^[150]

From this perspective, a joint quantitative assessment and ML-aided analysis of 140 representative catalytic systems for electrocatalytic nitrogen fixation indicate that MXenes and MXene-based hybrids, along with noble-metal-based catalysts, typically show poorer overall performance, mainly because of their scarcity and increased material expenses. This class-based comparison reinforces that future catalyst development must thoughtfully balance catalytic performance, faradaic efficiency, and material cost for feasible scale-up and practical application.^[153]

Moreover, using novel electrocatalysts, such as multi-metallic MXene, offers a novel method that uses light for improved $\text{eNO}_3\text{-RR}$ efficiency, but their long-term stability and production costs may pose challenges. Meanwhile, a comprehensive approach that

incorporates LCA and TEA is crucial for evaluating the ecological and economic viability of these materials.^[152]

On the other hand, electricity costs dominate, and at current renewable energy prices, electrochemical NH_3 production struggles to compete with the Haber-Bosch process. Only under very low renewable electricity costs ($< \$0.024$ per kWh), high FE, and substantial production rates does the economics approach parity.^[150]

In conclusion, the current technology readiness level (TRL) of NO_3^- RR remains at 3-4, requiring advances in catalyst design, reactor scaling, and process integration. Additionally, most reported TEA models still fail to account for the complexities of real wastewater, such as anion/cation interactions, coexisting organics, and pH variations. Future initiatives must improve evaluations of system integration to support industrial applications.^[151] Tackling these interdisciplinary issues is crucial to transform MXene-based technologies from promising lab concepts into commercially viable systems for sustainable, large-scale NH_3 production.^[154]

7. Key Challenges

Although the electrocatalytic nitrate reduction process offers promising advantages compared with conventional ammonia generation methods, several challenges remain before widespread implementation. Technology is still in its early stages compared with the century-old, highly optimized H-B process or the decades of research on NO_3^- reduction to N_2 and NH_3 . Long-term durability data, standardized performance benchmarks, and detailed catalyst characterization under practical operating conditions remain the most important technical issues. Furthermore, the hydrogen evolution side-reaction becomes more pronounced at low NO_3^- concentrations, raising safety and efficiency concerns at scale. Technically, treating the large volumes of wastewater required to achieve meaningful NH_3 output would necessitate oversized reactors and extended reaction times unless nitrate is pre-concentrated, an area that requires additional research. To date, few studies have examined the performance of electrocatalysts with real wastewater matrices from diverse sources, making it difficult to identify optimal feedstock.

Importantly, early techno-economic assessments indicate that developed catalysts toward eNO_3^- RR can already compete with existing electrochemical NH_3

production routes, with projected fertilizer costs potentially approaching those of the H-B process. The renewed interest in nitrate electroreduction, therefore, represents a viable pathway toward sustainable NH_3 generation. Realizing this potential will require systematic studies on catalyst stability, process integration, capital and operational costs, wastewater logistics, and downstream product separation. Establishing consistent reporting protocols and conducting rigorous, large-scale demonstrations will be essential for fully evaluating the feasibility and environmental impact of this emerging technology.

Notwithstanding these difficulties, from a data-centered design viewpoint, the use of ML in MXene-based eNO_3^- RR catalysts is still in its early stages, with only a small number of studies conducted so far. This discrepancy mainly arises from the lack of extensive, uniform datasets covering various MXene compositions, terminations, and dopant/vacancy arrangements, along with a deficiency of descriptor libraries designed specifically for MXene surface chemistry. As a result, the majority of documented ML initiatives depend on small, single-study datasets, restricting the transferability of models among various MXene families. To bridge this gap, coordinated efforts are needed to establish common, standardized DFT and experimental databases for MXene-related nitrate electroreduction, as well as to create MXene-specific descriptors that can apply broadly across different compositions.

In summary, upcoming research on eNO_3^- RR process using MXene-based catalysts will likely face challenges in structural optimization, dynamic simulation, MXenes characterization, economic factors, and associated environmental impacts, as schematically shown in **Fig. 17**.^[28, 36, 40, 63, 155-157]

8. Conclusions

MXene-based electrocatalysts offer a sustainable route to convert nitrogenous waste into NH_3 through the electrochemical nitrate reduction reaction. This approach can lower the carbon footprint of conventional NH_3 production while recycling NO_3^- from wastewater and other environmental sources. This review covered the reaction mechanisms, state-of-the-art MXene-based catalysts, and machine-learning-assisted modeling of NH_3 generation, and it outlines directions for future development.

The reported achievements have demonstrated that eNO_3^- RR is a promising route to achieve the N-cycle

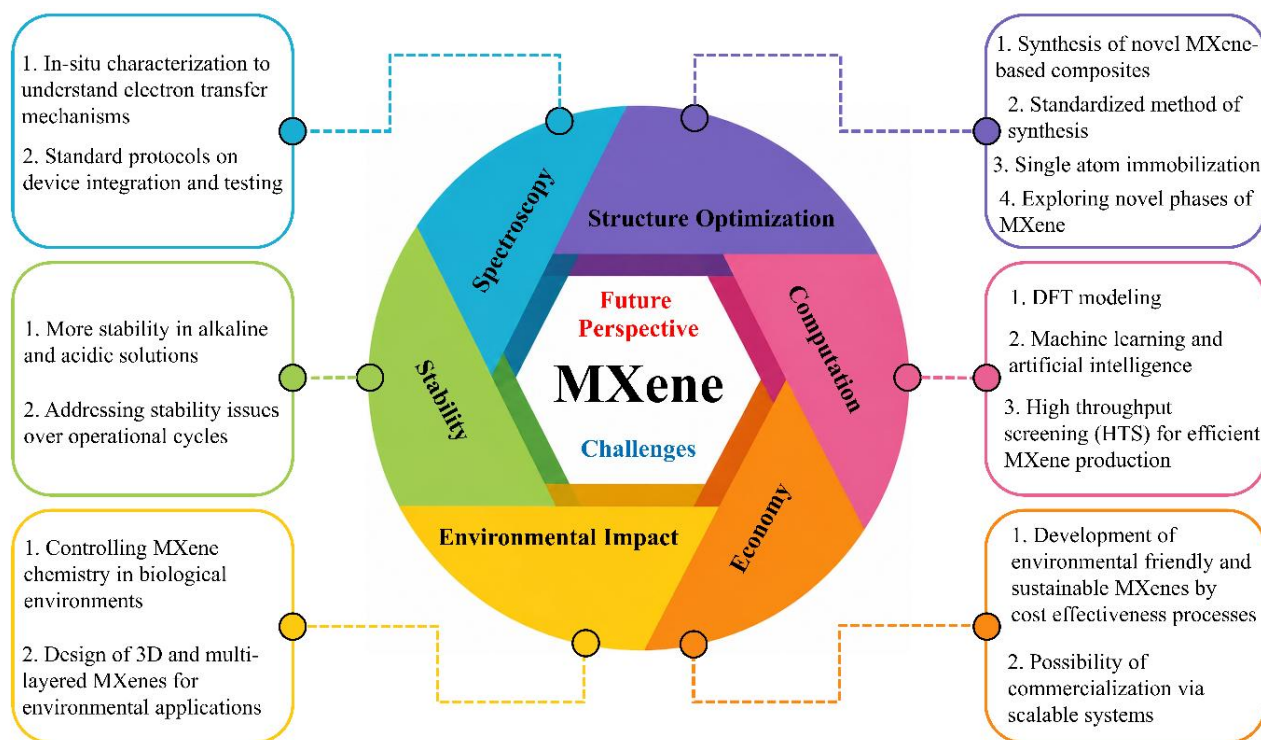


Figure 17. The trajectory of upcoming research on $e\text{NO}_3^-$ RR to generate NH_3 using MXenes through electrocatalysis.

goal under environmental conditions, and multiple catalytic strategies have been proposed to enhance ammonia yield and selectivity. However, there are fundamental challenges as follows:

(i) From a practical perspective, $e\text{NO}_3^-$ RR technology still lacks electrocatalysts that combine high activity, selectivity, and long-term durability under industrially relevant conditions. A further challenge is the substantial co-generation of H_2 as a side product during electrolysis, which is typically vented and poses safety and efficiency concerns. Addressing these issues through catalyst and system engineering will be essential before $e\text{NO}_3^-$ RR can be deployed at scale.

(ii) Variations in experimental parameters, including electrolyte pH, nitrate concentration, and other operational details, strongly influence catalytic activity and selectivity, yet their systematic effects are insufficiently understood. This lack of standardization leads to incomparable results across studies and hinders collective progress. The establishment of benchmark catalysts and unified testing protocols is therefore a priority for the $e\text{NO}_3^-$ RR community.

Overall, while electrochemical nitrate-to-ammonia conversion holds great potential for sustainable nitrogen management, realizing its full promise will

require coordinated advances in fundamental understanding, materials development, process integration, and standardization. Consequently, research should focus more on practical application scenarios and cost-effectiveness, while broadening ML-based descriptor identification tailored to MXene chemistries, to connect fundamental lab studies with real-world application.

CRedit authorship contribution statement

Sayed Majid Ghoreishian: Conceptualization, Writing - review & editing, Writing - original draft. **Masoom Ghasemi:** Formal analysis, Data curation. **Nasrollah Hamidi:** Writing - review & editing. **Jianhu Tong:** Conceptualization, Writing - review & editing. **H. Bryan Riley:** Conceptualization, Writing - review & editing, Funding acquisition.

Declaration of competing interest

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

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