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Next-generation nitrogen fixation strategy: empowering electrocatalysis with MXenes

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In recent years, the development of sustainable and cost-effective electrocatalysts for nitrogen (N_2) fixation has garnered significant attention, leading to the introduction of next-generation materials with electrocatalytic properties. Among the most interesting types of these materials, MXenes and their composite forms with their unique properties like high electrochemical activity, large surface area, tunable properties, excellent electrical conductivity, chemical stability, and abundant transition metals have been widely explored. These properties make MXenes promising candidates for various electrochemical reactions, including water splitting, oxygen reduction, hydrogen evolution, N_2 activation and reduction, among others. The interface of these materials could be engineered with other entities which can serve as a promising tool for sustainable production of ammonia (NH_3) to address the global nitrogen-related challenges. Moreover, optimizing the interfaces between them and reactants is another way to achieve high catalytic activity, selectivity, and stability. Accordingly, this review aims to offer a comprehensive overview of the current state of research in the field of electrocatalytic N_2 fixation deploying MXenes and their composites. The highlights comprise progress made in understanding the catalytic properties and unique performances of MXenes for N_2 fixation, as well as challenges that persist in this context and the possible solutions that could be implemented to circumvent these challenges in the future.

1. Introduction

Nitrogen (N_2) fixation, the conversion of atmospheric N_2 into chemically useful compounds, plays a pivotal role in the global nitrogen cycle and is crucial for sustaining life on Earth. Traditionally, N_2 fixation has been largely achieved through the energy-intensive Haber–Bosch process, which operates at high temperatures and pressures.[1–3] However, the use of traditional techniques for commercial purposes is hindered by several factors such as low faradaic efficiency, suboptimal ammonia yield, and high overpotential caused by the presence of the strong $N\equiv N$ bond and the dominant competing hydrogen evolution reaction.[4]

In light of these challenges, electrocatalytic N_2 fixation has emerged as a promising alternative that offers several advantages. This approach harnesses electricity to drive the conversion of N_2 to ammonia (NH_3) or other valuable nitrogen-containing compounds.[5] By utilizing electrocatalysis, it is possible to achieve a more sustainable and environmentally friendly process compared to conventional N_2 fixation methods.

Efficient electrocatalytic N_2 fixation requires the design and development of highly active catalysts, typically comprising transition metals such as iron, cobalt, or molybdenum, which facilitate the electrochemical reduction of N_2. The pursuit for efficient catalysts with high selectivity and stability is a critical aspect of research in this domain.[3] Electrocatalytic N_2 fixation can be achieved through various electrochemical processes, including electrochemical reduction and electrochemical nitrogenation. These processes necessitate the use of different reaction mechanisms and distinct electrochemical setups, thus enabling researchers to explore a wide range of strategies and optimize their performances.[6,7]

While electrocatalytic N_2 fixation holds great promise, several challenges need to be addressed for its widespread implementation. Key challenges include the development of efficient catalysts, understanding the underlying reaction

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mechanisms, and optimizing the reaction conditions.[8] In addition, the scalability of the process and its integration with renewable energy sources must be considered to realize its full potential.[9,10]

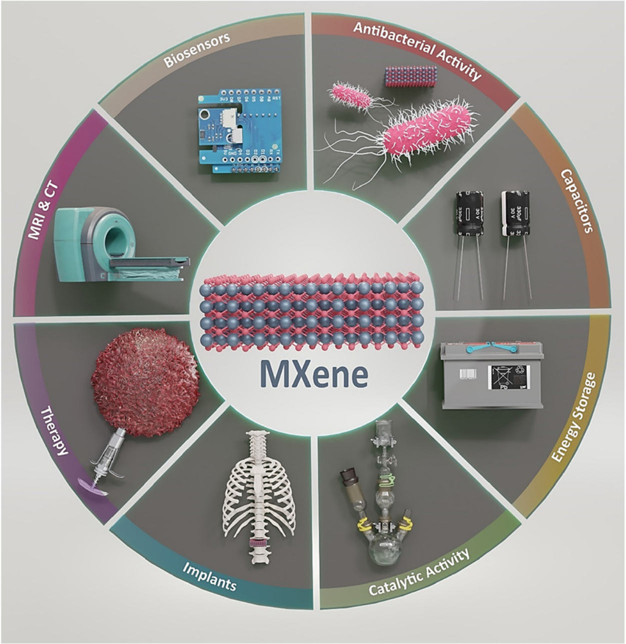
Electrocatalytic N_2 fixation has significant potential for developing fertilizers and other nitrogen-based chemicals.[11] By enabling on-site N_2 fixation using renewable energy sources, this technology can contribute to a more sustainable and decentralized approach for nitrogen fixation. Therefore, electrocatalytic N_2 fixation can reduce dependence on fossil fuels and mitigate the environmental impact associated with traditional N_2 fixation processes.

Current methods of electrochemical nitrogen fixation face limitations in achieving high ammonia yields due to the simultaneous occurrence of the hydrogen evolution reaction. To overcome these obstacles, ongoing research focuses on developing high-performance electrocatalysts to enhance the viability and efficiency of electrocatalytic N_2 fixation.[6,12] For instance, boron carbide nanosheets, as metal-free catalyst, are demonstrated as ideal materials for the electrochemical fixation of nitrogen-to-ammonia at ambient conditions with remarkable performance.[13] With an impressive ammonia yield (~26.57 μg h^{-1} $mg_{cat.}{}^{-1}$) and a notably high faradaic efficiency (~15.95%) at −0.75 V *versus* the reversible hydrogen electrode, they can be considered among the most active electrocatalysts for aqueous-based nitrogen reduction reactions.[13]

MXenes are a fascinating class of two-dimensional (2D) materials, composed of metal carbides, nitrides, and carbonitrides materials. These materials have gained significant attention in the field of materials science and nanotechnology. The name "MXenes" is derived from their characteristic structure, where "M" represents the transition metal and "X" represents carbon and/or nitrogen. Their general formula is $M_{n+1}X_nT_x$ (n = 1–4), where "T" is attributed to their surface functional groups.[14–16]

MXenes are typically synthesized through a process called etching, which begins with a layered parent material, such as MAX phases (*e.g.*, Ti_3AlC_2). The etching process selectively remove the "A" layer, resulting in a 2D MXene structure. Various etching agents. such as hydrofluoric acid (HF) or strong alkaline solutions, can be used to obtain specific MXene compositions.[17,18] Currently, the synthesis of MXenes has been a topic of extensive research, with a growing emphasis on developing environmentally benign techniques. By exploring alternative etchants, solid-state intercalation reactions, and sustainable solvents and surfactants, researchers are striving to achieve MXene synthesis methods that are both efficient and eco-friendly. These efforts contribute to the advancement of MXene research and pave the way for their widespread deployment in various industries.[19–21]

The specific sandwich structure of MXenes provides them with exceptional properties, including high electrical conductivity, good mechanical strength, and excellent thermal stability.[22,23] In addition, their high surface area makes them suitable for diverse applications, such as energy storage, catalysis, biomedicine, and electronics (Scheme 1).[24–26] MXenes also exhibit excellent electrocatalytic activity, making them promising candidates for water splitting and fuel cell applications.[27,28]



Scheme 1 Different applications of MXene based materials.

MXenes hold significant importance in electrocatalytic N_2 fixation due to their highly active catalytic nature, tunable surface chemistry, electrical conductivity, stability, and the ability to integrate with other materials.[29] MXene-based electrocatalysts have the potential to minimize the environmental footprint associated with N_2 fixation. Additionally, their efficient catalytic activity can reduce the energy consumption and waste generation typically associated with traditional nitrogen fixation methods.

Typically, the N_2 fixation process could proceed *via* four different pathways including distal, alternating, enzymatic, and mixed mechanisms, all of which involve six sequential hydrogenation steps ($N_2 + 6H^+ + 6^{e-} \rightarrow 2NH_3$). In the distal mechanism for an end-on adsorbed N_2 molecule, the distant nitrogen atom undergoes hydrogenation by three proton–electron pairs, leading to the release of the first NH_3. Conversely, the alternating mechanism involves six consecutive proton–electron pairs acting on the two nitrogen atoms alternately. When the N_2 fixation follows the enzymatic mechanism, proton–electron pairs are alternately added to both nitrogen atoms of a side-on adsorbed N_2 molecule. Furthermore, a mixed mechanism may occur where $*N_xH_y$ species transition between distal and alternating mechanisms.[30]

This review aims to highlight the potential applications of MXenes in electrocatalytic N_2 fixation and their importance in the context of sustainable chemistry. By examining the advantages and current limitations associated with MXene-based electrocatalysts, this appraisal sheds light on the feasibility of using MXenes as efficient and environmentally friendly alternatives to conventional N_2 fixation methods.

2. Fundamentals of electrocatalytic N_2 fixation

2.1. N_2 fixation methods

The N_2 fixation, *via* natural or industrial processes, involves the conversion of atmospheric nitrogen (N_2) into chemically usable forms, such as ammonia (NH_3), which can be utilized by living organisms. These processes are crucial for the cycling of nitrogen and the sustainability of life on Earth.[31] There are two main mechanisms for N_2 fixation, (a) natural process, in which certain microorganisms, such as nitrogen-fixing bacteria (*e.g.*, *Rhizobium*, *Azotobacter*, and *cyanobacteria*), have converted N_2 into ammonia through a process called biological nitrogen fixation (BNF). These bacteria possess the enzyme nitrogenase, which catalyzes the conversion of N_2 into NH_3 using energy from adenosine triphosphate (ATP) and a reducing agent, usually in the form of electrons from photosynthesis or respiration.[32,33] Moreover, atmospheric lightning discharges can facilitate N_2 fixation by providing the energy required for breaking the strong nitrogen–nitrogen triple bond. The lightning-induced high temperatures and pressures create favorable conditions for the formation of nitrogen oxides (NO_x), which can dissolve in rainwater and eventually get converted to nitrate ions (NO_3^-) in the soil.[1,34]

The industrial process of N_2 fixation is predominantly carried out using the Haber–Bosch process. This process involves the reaction of N_2 and hydrogen (H_2) under high temperature (400–500 °C) and pressure (150–250 atmospheres) in the presence of an iron-based catalyst. The reaction produces ammonia (NH_3), which can then be further processed to produce fertilizers and other nitrogen-based chemicals.[35,36] Electrochemical methods have emerged as a promising alternative for N_2 fixation wherein deployment of an electrocatalyst, such as certain transition metals or MXenes, and an electric current, facilitate in reducing N_2 to NH_3 or other nitrogen-containing compounds. Electrochemical N_2 fixation has the potential to be a more sustainable and energy-efficient process, especially when coupled with renewable energy sources.[35] Not surprisingly, considerable attention has recently been directed towards the development of electrochemical N_2 fixation as an eco-friendly method for generating ammonia.[7] The objective is to tackle the significant energy requirement and carbon emissions that are typically associated with the traditional Haber–Bosch process. However, electrochemical N_2 reduction presents several obstacles, including the limited solubility of nitrogen in aqueous solutions, sluggish kinetics, and the inherent competition from the hydrogen evolution reaction. Notwithstanding these challenges, remarkable strides have been made in the advancement of heterogeneous electrocatalysts and lithium-mediated approaches to enhance production rates for ammonia.[7,37]

2.2 Challenges and limitations in N_2 fixation

There are several challenges and limitations related to the N_2 fixation which are arising from the strong triple bond between nitrogen atoms in N_2 and the energy-intensive nature of breaking this bond. The following aspects ought to be addressed:

High energy requirements. Breaking the strong triple bond in N_2 requires a significant amount of energy. Traditional industrial processes, such as the Haber–Bosch process, rely on high temperatures and pressures, leading to the substantial energy consumption. In addition, plasma-assisted nitrogen fixation is widely regarded as a sustainable and eco-friendly alternative to the traditional Haber–Bosch process, although still has deficiency in high energy consumption and limited production rates. According to a recent innovative study, it has been shown that the non-thermal enhancement of arc plasma can significantly decrease the energy requirements for nitrogen fixation while attaining high selectivity of NO and minimizing energy consumption.[38] The quest for alternative and sustainable methods that can reduce the energy requirements for N_2 fixation has been a major challenge.[39]

Cost of catalysts. The use of catalysts is crucial in N_2 fixation processes to facilitate the conversion of N_2 to chemically useful compounds. However, many catalysts, such as those based on transition metals, are expensive with limited availability. Thus, identification and development of cost-effective catalysts that exhibit high activity, selectivity, and stability is an important task.[9,13]

Selectivity. Attainment of high selectivity in N_2 fixation processes is demanding since N_2 molecules can undergo various side reactions that lead to the formation of unwanted by-products.[9] Controlling the reaction conditions and developing catalysts that can selectively convert N_2 to desired nitrogen-containing compounds, such as NH_3, has been an arduous and ongoing task. For instance, a groundbreaking method has been introduced in a study for the synthesis of ammonia from N_2 using iridium and molybdenum catalysts, that could be performed under ambient reaction conditions under visible light irradiation.[40]

Sustainability and environmental impact. Traditional N_2 fixation processes rely heavily on fossil fuels as a source of hydrogen (H_2) for the reduction of N_2, which contributes to greenhouse gas emissions with substantial environmental impact. Therefore, it is crucial to develop more sustainable and eco-friendly N_2 fixation processes that exploit renewable energy sources and electrocatalytic methods.[37,41]

Scale-up and implementation. Transitioning from laboratory-scale to large-scale N_2 fixation processes presents its own set of hurdles. Scaling up of the prospective processes while maintaining efficiency, selectivity, and minimizing environmental impact requires careful engineering and optimization, and could be complex and even costly endeavor.

Biological limitations. Although biological N_2 fixation by certain microorganisms is a natural process, it is limited to specific organisms and environmental conditions. Expanding the range of organisms with the innate ability for biological nitrogen fixation and enhancing their efficiency in different ecosystems has been an ongoing trial. To optimize biological N_2 fixation, it is essential to have a comprehensive understanding of the various nitrogen-fixing microorganisms, their fixation mechanisms, and careful selection of highly efficient N_2 fixing microorganisms as biofertilizers.[32]

Addressing these contests and limitations requires interdisciplinary research efforts, including the development of novel catalysts, exploring alternative reaction conditions, optimizing energy efficiency, and integrating sustainable practices into N_2 fixation processes. In this context, exploration of new electrochemical methods, such as electrocatalytic N_2 fixation via the deployment of MXenes, offers potential for more sustainable and environmentally friendly nitrogen fixation processes in the future.

3. Sustainable synthesis of MXenes

As mentioned earlier, MXenes are a class of 2D nanostructures composed of $M_{n+1}X_nT_x$ that have attracted significant interest due to their extensive applicability in various fields such as optics, electronics, energy storage, conversion, environmental applications, catalysis, biotechnology, and medicine. Their unique properties, influenced by their carbon and/or nitrogen content, make them highly versatile. However, challenges related to the presence of transition metals need to be addressed to fully harness their potential.

To enhance the feasibility of MXenes, particularly for applications in biotechnology, environmental science, and energy-related fields, it is crucial to modify their composition and employ greener synthesis technologies during fabrication. By adopting more sustainable synthesis methods, it is possible to produce MXenes in a manner that is both efficient and environmentally friendly.[42,43]

The synthesis methods used for the fabrication of MXenes are categorized into two main classes: top-down methods and bottom-up approaches, the latter being deployed abundantly.[44] The etching method is the most prevalent method for preparing MXenes, which involves the use of toxic acids like hydrofluoric (HF) acid or mixture of HCl and lithium fluoride (LiF).[17] In order to reduce the use of hazardous materials like HF, other top-down and bottom-up techniques have been introduced in recent years. These procedures include chemical vapor deposition, hydrothermal, electrochemical etching, microwave-assisted synthesis, molten salt etching, and UV-induced selective etching.[43,45–47] Thus, there is a pressing need for the development of green and sustainable synthesis techniques that can produce high-quality MXenes with minimal environmental footprint.[45,48]

Additional techniques have also been introduced to prevent the use of alkali, acid, or fluorine compounds. These methods include liquid-phase laser ablation, probe sonication, and physical vacuum distillation. Advanced methods such as microwave-assisted synthesis and electrochemical exfoliation offer rapid and controlled production of MXenes, enabling precise tuning of MXene properties, such as thickness and surface chemistry, for various applications. Furthermore, continuous flow synthesis systems can enhance the reproducibility and yield of MXene production.[47,49–51]

However, it is important to mention that the synthesis methods for MXenes represent a double-edged sword. While chemical etching is popular, its environmental impact cannot be ignored. Hydrothermal synthesis, on the other hand, offers a greener alternative but might come with its own set of challenges, such as lower yields. The trade-offs amongst different synthesis approaches in terms of cost, environmental impact, and material quality, need to be critically assessed, wherein the limited availability of sustainable precursors that meet the purity and reactivity requirements for MXene production are of paramount importance.[52]

The development of alternative sources of precursors that are both eco-friendly and cost-effective is crucial for advancing green synthesis methods. Another challenge lies in optimizing reaction conditions to ensure high yield and reproducibility while minimizing energy consumption and waste generation. Fine-tuning synthesis parameters such as temperature, reaction time, and solvent choice is essential for achieving consistent results in an environmentally friendly manner. Furthermore, scaling up greener MXene synthesis processes from laboratory-scale to industrial production poses additional challenges in terms of cost and efficiency. Designing efficient and sustainable production facilities that adhere to green chemistry principles will be essential for overcoming these challenges and establishment of greener MXene synthesis as a viable industrial practice.[53,54]

Researchers are actively exploring novel approaches to enhance the eco-friendliness and efficiency of MXene production. One promising avenue is the development of bio-inspired synthesis methods that mimic natural processes to create MXenes with minimal environmental impact. By drawing inspiration from biological systems, researchers aim to design innovative pathways for synthesizing MXenes using renewable resources and bio-compatible reagents.[19,20] Moreover, the integration of artificial intelligence and machine learning algorithms in the optimization of greener MXene synthesis processes is expected to advance material design and discovery. By leveraging computational tools to predict optimal reaction conditions, precursor combinations, and synthesis pathways, researchers can accelerate the development of sustainable MXene materials for various applications.[55,56] Another key aspect of future perspectives in green MXene synthesis is the exploration of additive manufacturing techniques, such as 3D printing, for on-demand and customized production of MXene-based devices.[57,58] By combining greener synthesis methods with advanced manufacturing technologies, researchers can unlock new possibilities for creating complex MXene structures with tailored properties for specific applications.

4. MXenes based composite as electrocatalysts for N_2 fixation

Electrocatalysts play a crucial role in the process of N2 fixation by accelerating chemical reactions at the electrode–electrolyte interface. They facilitate the conversion of N_2 molecules into reactive nitrogen species that can be further reduced to NH_3, and is obligatory for the production of fertilizers and the sustenance of life on Earth.[13] These catalysts play a vital role in overcoming the high energy barrier associated with the cleavage of stable triple bond of N_2 by enhancing the reactivity of N_2 *via* an alternative reaction pathway with lower activation energy. They achieve this by promoting the adsorption of N_2 molecules on the electrode surface and facilitating their subsequent reduction steps.

The choice of an appropriate electrocatalyst is crucial as it determines the efficiency and selectivity of N_2 fixation. Various types of electrocatalysts have been investigated for N_2 fixation, including transition metals, metal alloys, metal–organic frameworks, and metal-free catalysts.[59–62] Each type exhibits distinct catalytic properties and has its own advantages and limitations. The selection of an electrocatalyst depends on factors such as its ability to adsorb and activate N_2 molecules, its stability under electrochemical conditions, and importantly, the cost-effectiveness.[6,12]

For instance, Ren *et al.*[63] discovered that the Mo_2C nanorods had exceptional electrocatalytic properties as an N_2 reduction reaction (NRR) catalyst for synthesizing NH_3 through artificial N_2 fixation. This catalyst exhibited remarkable durability and satisfactory selectivity under ambient conditions, showing an impressive faradaic efficiency of ~8.13% and NH_3 yield of 95.1 μg h^{-1} $mg_{cat.}{}^{-1}$ at −0.3 V in 0.1 M HCl.[63] This research has offered an alternative sustainable approach for nitrogen fixation. Application of Mo_2C nanorods as an electrocatalyst for the electrochemical conversion of N_2 to NH_3 presents a promising way for carbon-free NH_3 production, which is significant for reducing CO_2 emissions and achieving sustainable nitrogen fixation.

In another study, the $FeMoO_4$ nanorods exhibited intriguing NRR activity, resulting in the NH_3 yield of 45.8 μg h^{-1} $mg_{cat.}{}^{-1}$ at −0.5 V, along with a notable faradaic efficiency of ~13.2% at −0.3 V.[64] Through mechanistic studies, it was uncovered that the combined presence of Fe and Mo played a synergistic role in enhancing N_2 adsorption and facilitating electron transfer on $FeMoO_4$. Notably, the unsaturated 3-fold coordinated Mo (Mo_{3c}) sites emerged as the primary active centers responsible for stabilizing the crucial $^*N_2H$ intermediate and thus reducing the energy barrier of the reaction.[64] This study revealed high efficiency in the production of NH_3 which renders it an attractive candidate for industrial applications where efficient ammonia synthesis is desired. Moreover, the notable amounts of faradaic efficiency suggested that a significant portion of the electrons was being effectively utilized for the NRR process. Besides, the identification of unsaturated 3-fold coordinated Mo (Mo3c) sites as the primary active centers for stabilizing the intermediate components are very important since these sites are responsible for reducing the energy barrier of the reaction, and enhancing the catalytic activity of $FeMoO_4$ nanorods.

MXenes and their composites exhibit high electrochemical activity, which is crucial for the reduction of N_2 during the electrocatalytic N_2 fixation process.[65,66] Their unique properties, such as high surface area and tunable surface chemistry, make them promising candidates for addressing the limitations associated with this critical process.[65,67,68] Recently, several MXene-based electrocatalysts have been designed for N_2 fixation and NH_3 production with high efficiency and selectivity (Table 1).

The extensive literature in this area provides a comprehensive understanding of the various strategies employed to enhance the electrocatalytic performance of MXenes. These studies explore a range of approaches, from the development of novel MXene composites to surface functionalization and hybridization with other materials, thus showcasing the versatility and potential of MXenes in this field. For instance, Xu *et al.*[69] developed a novel electrocatalytic nitrogen fixation catalyst, namely 1T-MoS_2 nanospots assembled on conductive MXene (Ti_3C_2) (Fig. 1). The as-prepared composite exhibited remarkable activity and selectivity for the nitrogen reduction reaction. As a result, the composite achieved a faradaic efficiency of ~10.94% and a NH_3 yield rate of 30.33 μg h^{-1} $mg_{cat.}{}^{-1}$. Moreover, the 1T-MoS_2@Ti_3C_2 composite demonstrated excellent stability and durability throughout the recycling assessment. The synergistic effects between 1T-MoS_2 and MXene led to a high-performance electrocatalytic N_2 fixation reaction.[69] While the faradaic efficiency of this study was not so high, the higher selectivity, high stability, and the ability to maintain performance over multiple cycles boosted the practicality of the catalyst.

Cao *et al.*[70] conducted a systematic investigation on the electrocatalytic N_2 fixation using transition metal atoms (Fe, Co, Mo, Ru) anchored on defected V_2C using first-principles calculations. Their calculated results demonstrated that the overpotential of NRR on Mo-doped V_2C was only 0.49 eV along the mixed enzyme pathway, which was substantially lower compared to the pristine V_2C (0.61 eV). This remarkable reduction in overpotential was attributed to the synergistic effect between Mo and V, thus promoting the activation of N_2 molecules. In addition, the adsorption of N_2 on Mo-doped V_2C was significantly higher than that of H^+, effectively inhibiting the hydrogen evolution reaction. The exceptionally low overpotential and favorable selectivity established Mo/V_2C as a promising catalyst with good stability and enhanced performance for NRR.[70] Herein, authors introduced a sustainable and efficient approach for nitrogen fixation. The significantly greater adsorption of nitrogen compared to H^+ suggests effective inhibition of the hydrogen evolution reaction (HER), leading to superior selectivity towards NRR.

The presence of transition metal atoms in the MXene layers offers active sites for the adsorption and activation of N_2 molecules and facilitates their subsequent reduction to NH_3; thus, the enhanced activity of MXenes contributes to the efficient conversion of N_2 into valuable NH_3.[95] For instance, the feasibility of deploying a transition metal atom supported on $Ti_3C_2T_2$ MXene with O/OH terminations was explored as a

Table 1 Some selected examples of MXene-based composites for electrocatalytic N_2 fixation

MXene-based composites	faradaic efficiency	Ammoniac yield	Properties	Ref.
Boron nitride quantum dots/ MXene ($Ti_3C_2T_x$) heterostructures	19.1 ± 1.6%	52.8 ± 3.3 μg h^{-1} mg^{-1}	• Improving the electron-donating capability of heterostructure due to the electronic interactions between two structures • High N_2-to-NH_3 selectivity due to the blocking the active site of MXene by BNQDs	71
MXene (Ti_3C_2)/MAX heterostructures	36.9%	2.73 μg h^{-1} cm^{-2}	• Fixation of N_2 using electrochemical method • Providing an excellent MXene/MAX structure with high center for management of N_2 fixation • Transferring electrons from MAX phase into the MXene phase • Improved electrical conductivity and electrocatalytic performance	72
Three-dimensional (3D) $Ti_{3-x}C_2T_y$ MXene	9.87%	24.33 μg h^{-1} mg^{-1}	• Excellent vacancy-tunable N-doped catalyst • Adjustment of the Ti^{3+} species to facilitated Ti^{3+}-N_2 d-pπ-back donation interactions • Efficient electrochemical N_2 fixation	29
MnO_2-$Ti_3C_2T_x$ MXene nanohybrids	11.39%	34.12 μg h^{-1} mg_{cat}^{-1}	• Efficient electrocatalyst for the NRR; robust durability • Fabrication of NH_3 using electrochemical method using a cheap catalyst. • High selectivity of MnO_2–MXene for NH_3 production due to the presence of unsaturated Mn	73
MXene-derived nanocomposites	13.3%	14.0 μg h^{-1} cm^{-2}	• Excellent electrochemical stability • High NRR activity resulted from the good distribution of TiO_2 phase on carbon layer and exposing the active site	74
MXene/$TiFeO_x$-700	25.44	2.19 μg h^{-1} cm^{-2}	• Efficient electrochemical conversion of N_2 to NH_3 due to the presence of high surface reactivity resulted from decreasing the inactive F*/OH*terminals and eliminating the surface work function	75
Fluorine-free $Ti_3C_2T_x$ nanosheets	9.1%	36.9 μg h^{-1} $mg_{cat.}^{-1}$	• Enhanced electrocatalytic NRR resulted from the effect of size and fluorine free feature	76
OH–Ti_3C_2	7.01% (at 20 °C) 9.03% (at 60 °C)	1.71 μg h^{-1} cm^{-2} 12.46 μg h^{-1} cm^{-2}	• Facilitating the electron transfer, surface adsorption and activation of dinitrogen due to the surface hydroxyl modification	77
Cu/$Ti_3C_2T_x$ nanosheets	7.31%	3.04 μg h^{-1} cm^{-2}	• Excellent electrochemical stability and durability • Wider conduction and valence band and a larger Fermi level compared with Ti_3C_2 • Enhancement in catalytic activity and conductivity due to the presence of Cu	78
CuAg/$Ti_3C_2T_x$ nanosheets	9.77%	4.12 μmol cm^{-2} h^{-1}	• High stability and selectivity • Improving the catalytic activity and electrical conductivity due to the presence of CuAg	79
TiO_2/$Ti_3C_2T_x$ nanosheets	16.07%	32.17 μg h^{-1} $mg_{cat.}^{-1}$	• Reversible hydrogen electrode • Enhanced electrochemical NRR	80
Ruthenium (Ru)@Ti_3C_2	13.13%	2.3 μmol h^{-1} cm^{-2}	• High selectivity and high electrocatalytic performance • Production of NH_3 under the environmental conditions	81
Ru@Ti_3C_2	23.3 %	27.56 μg h^{-1} mg^{-1}	• Good dispersity of Ru on Ti_3C_2O • Ru act as active site for catalytic reaction • High selectivity with superior catalytic activity	82
Zeolitic imidazolate framework (ZIF)-67@Ti_3C_2 composites	20.2%	6.52 μmol h^{-1} cm^{-2}	• Enhanced electrocatalytic activity with high selectivity due to the synergistic effect between ZIF and MXene	83
Fluorine-terminating MXene ($Ti_3C_2T_x$)	7.4%	2.81×10^{-5} μmol s^{-1} cm^{-2}	• Fabrication of surface functionalization toolkit MXenes with improved electrochemical catalytic ability	84
Antimony (Sb)/Nb_2CT_x	27.3%	49.8 μg h^{-1} mg^{-1}	• Enhanced electrocatalytic N_2 reduction, with high selectivity due to the presence of Sb, which provides high active site	85
Ruthenium (Ru)–Mo_2CT_x	25.77%	40.57 μg h^{-1} mg^{-1}	• Enhanced electrocatalytic activity and reducing thermodynamic energy barrier	86
MXene (V_2CT_x) electrocatalysts	4%	12.6 μg h^{-1} mg^{-1}	• Exhibiting a low reaction barrier of 0.88 eV in the distal route for the catalyst	87
Boron nitride quantum dots decorated Nb_2CT_x-MXene	16.7%	66.3 μg h^{-1} mg^{-1}	• Excellent stability, decreasing the reaction energy barrier, and hindering evolution of H_2 • Synergistic enhancement in electrocatalytic N_2 reduction	88
Oxidized Nb_2CT_x MXenes	11.5%	29.1 μg h^{-1} $mg_{cat.}^{-1}$	• Improved selectivity of NRR due to the specific structural features of catalyst including the layered graphitic structure, reactive V_O, and the expanded interlayer space	89
TiO_2/$Ti_3C_2T_x$ MXene composites	44.68%	44.17 μg h^{-1} $mg_{cat.}^{-1}$	• Robust electrochemical durability and ideal selectivity and stability • Presence of TiO_2 leads to prevention of MXene micro-stacking and enhancement of MXene surface specific area	90

Table 1 *(Contd.)*

MXene-based composites	faradaic efficiency	Ammoniac yield	Properties	Ref.
$TiO_2/Ti_3C_2T_x$ nanohybrids	8.42%	26.32 μg h^{-1} mg^{-1}	• Fabrication of TiO_2 nanoparticles on the surface of MXene using hydrothermal method • Enhancing the NRR electrocatalyst property of MXene • Excellent electrochemical durability with good NH_3 selectivity	91
1T′-MoS_2/Ti_3C_2 composite	30.75%	31.96 μg h^{-1} mg^{-1}	• Good selectivity and stability without significant reducing in the amounts of ammonia production • Improving the NRR performance of 1T′-MoS_2 by adding MXene	92
O-vacancy-rich MoO_{3-x} anchored on MXene ($Ti_3C_2T_x$)	22.3%	95.8 μg h^{-1} mg^{-1}	• Utilizing the O-vacancies on MoO_{3-x} as active site for the chemisorption of N_2 and activate it • MXene optimized the affinity of NRR intermediates for bonding to the reduced energy barriers • Enhanced electrochemical NRR activity and improved selectivity	93
MXene ($Ti_3C_2T_x$) quantum dots/Cu nanocomposites	21.3%	78.5 μg h^{-1} mg^{-1}	• Synergistically enhanced electrocatalytic NRR activity due to providing the dual active sites of Cu-Ti dimer • Eliminating the reaction energy barrier and depressing the H_2 evolution reaction	94

single-atom catalyst for electrochemical N_2 reduction.[96] The catalytic performance of transition metal single atoms was evaluated based on their adsorption behavior on the MXene, as well as their ability to bind N_2 and desorb NH_3 molecules. It is worth noting that the OH terminations on MXene ($Ti_3C_2T_2$) could successfully increase N_2 adsorption and reduce NH_3 adsorption for single atoms. In here, authors chartered the surface functionalizing ability of MXenes for designing single-atom catalysts, from one side, and the first-principles calculations, which provides a solid theoretical foundation, from the other side to introduce a new catalyst for N_2 fixation and predict its function.[96]

In another study, Tang *et al.*[97] conducted an investigation into the potential use of a transition metal atom embedded on defective MXene nanosheets, specifically $Ti_{3-x}C_2O_y$ and $Ti_{2-x}CO_y$ with a Ti vacancy, as a single-atom electrocatalyst for the NRR (Fig. 2). Remarkably, the $Ti_{3-x}C_2O_y$ nanosheets with embedded Mo and W, as well as the $Ti_{2-x}C_2O_y$ nanosheets with entrenched Cr, Mo, and W, exhibited significant enhancement of the NRR while effectively suppressing the competitive hydrogen evolution reaction. Notably, the W/$Ti_{2-x}C_2O_y$ system demonstrated a particularly low limiting potential of −0.11 V wherein this outstanding performance could be attributed to the synergistic effects between the exposed Ti atom and the transition metal atom in the vicinity of an additional oxygen vacancy. The presence of embedded transition metal atoms allowed for the rational adjustment of polarization charges in the active center, thereby optimizing the binding strength of the crucial intermediate $^*N_2H$. Production of NH_3 from N_2 was initiated by the adsorption of $^*N_2$ followed by 3 protonation steps to fabricate the first NH_3 molecule, and then, 3 additional steps ensued to produce the other NH_3 molecule. These findings highlight the feasibility of preparing transition metal single-atom electrocatalysts on defective MXenes and their potential for achieving excellent NRR selectively over the competing hydrogen evolution reaction. Consequently, this opens up new opportunities for exploiting MXene-based single-atom electrocatalysts in NH_3 formation under ambient conditions.[97]

MXenes possess excellent electrical conductivity, allowing for efficient electron transfer during the electrocatalytic N_2 fixation process.[95,98] The advantages of MXenes in N_2 fixation, such as efficient electron transfer, tunable surface functionality, and synergistic interaction with co-catalysts, highlight their potential as effective electrocatalysts for this important reaction. The ability to tailor the properties of MXenes to enhance their catalytic performance is particularly promising for the development of efficient and selective electrocatalysts for N_2 fixation. The delocalized π-electrons in the 2D layers of MXenes enable rapid electron transport, minimizing the resistance and facilitating the transfer of electrons to the catalytic sites. This efficient electron transfer enhances the overall performance of MXenes as catalysts for N_2 fixation. The surface functionality of MXenes, such as hydroxyl or oxygen terminations, can be modified or functionalized to control the adsorption of N_2 molecules. This study offers significant insights into the design of efficient and economical catalysts for the electrochemical nitrogen reduction reaction (NRR) by investigating single-atom decorated v-Mo_2CT_2 MXenes with various terminations.[30]

The selective adsorption of N_2 on MXene surfaces is crucial for efficient activation of N_2 and subsequent reduction, which can be tailored by decorating the surface of MXenes with specific functional groups that have affinity for adsorption and activation of N_2 molecules. MXenes offer tunable electronic and structural properties, allowing for optimization of their catalytic performance in N_2 fixation. The composition, surface functionalization, and interlayer spacing of MXenes can be modified to match the specific requirements of the N_2 fixation reaction. This tunability enables the design of MXenes with enhanced catalytic activity, selectivity, and stability for efficient electrocatalytic N_2 fixation.

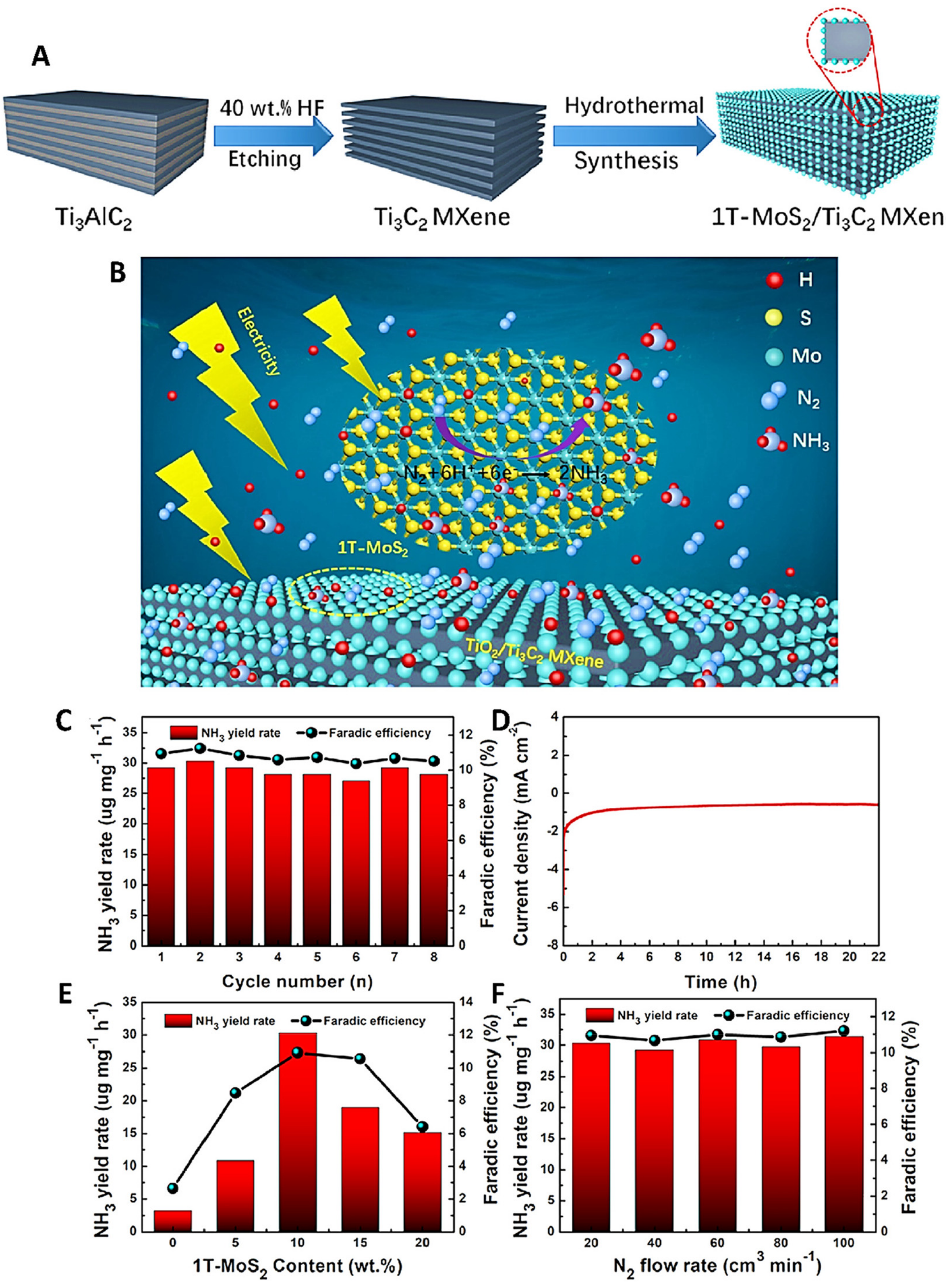


Fig. 1 (A) The preparative process of 1T-MoS_2@Ti_3C_2 composites for (B) high-performance electrocatalytic conversion of N_2 to NH_3. (C) The rates of NH_3 yield and faradaic efficiency of 1T-MoS_2@Ti_3C_2 composites (10 wt%) during recycling tests were examined. (D) The time–current density curves of MXene-based composites (10 wt%) were analyzed. (E) The NH_3 yield rates and faradaic efficiency of the MXene-based composites with varying content of 1T-MoS_2 quantum dots (0, 5, 10, 15, and 20 wt%) were measured. (F) The NH_3 yield rates and faradaic efficiency of the MXene-based composites (10 wt%) were evaluated under different N_2 flow rates at a potential of −0.3 V *vs.* reversible hydrogen electrode. Reproduced with permission from ref. 69. Copyright 2020 American Chemical Society.

MXenes can also play a role in facilitating the interaction between co-catalysts and N_2 molecules during N_2 fixation. The unique surface properties of MXenes, combined with their high electrochemical activity, can promote the adsorption and activation of co-catalysts, such as transition metal nanoparticles or molecular complexes. This synergistic interaction

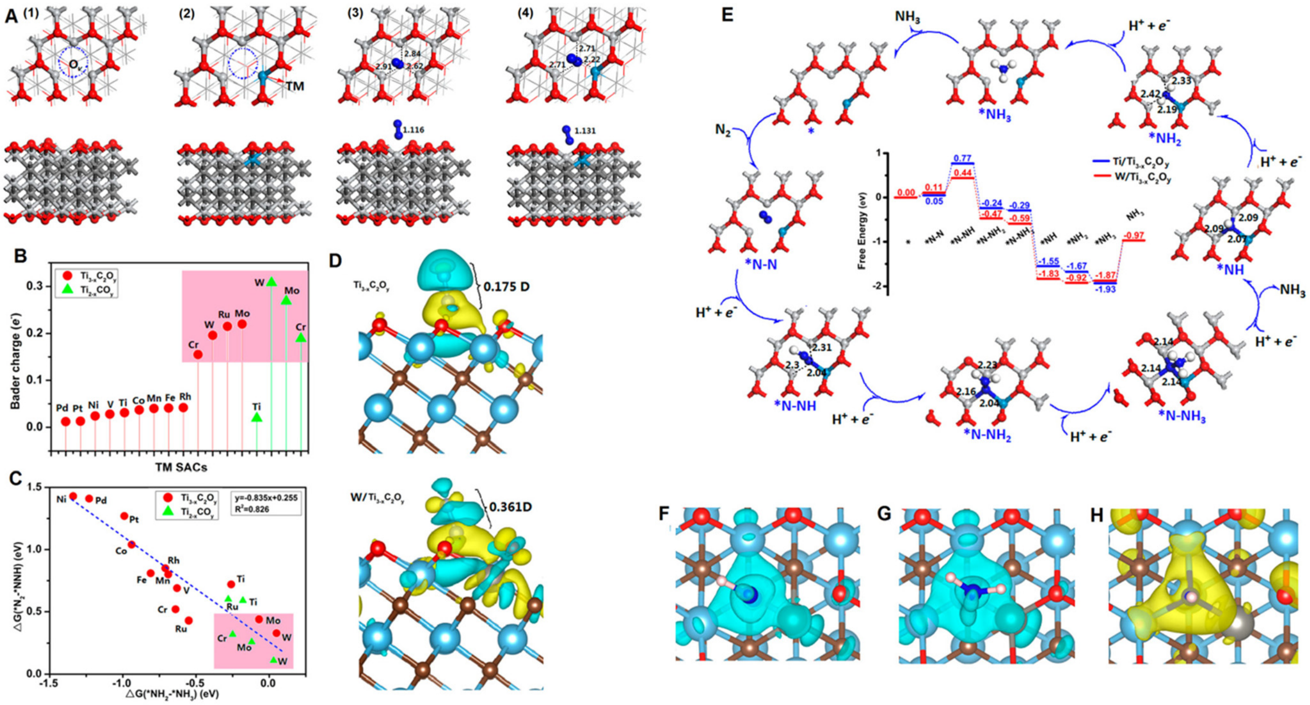


Fig. 2 (A) Top and side views of the geometrical structures of (**1**) Ti and (**2**) W/$Ti_{3-x}C_2O_y$ in the absence of gas adsorption (**1** and **2**), as well as with N_2 adsorption (**3** and **4**). All distances are expressed in angstroms. (B) The illustration showcases the transfer of electrons from transition metal/MXenes to the adsorbed N_2. (C) The scaling relationship between the free energy changes of the first and last hydrogenation steps in the context of NRR is examined. (D) The electron density differences resulting from N_2 adsorption on $Ti_{3-x}C_2O_y$, both with and without W doping. These differences are obtained by subtracting the electronic charges of the adsorbed N_2 and defective MXenes from transition metal/MXenes. The areas highlighted in yellow, and blue represent electron accumulation and depletion, respectively, with isosurface values of 0.001 e Å^{-3}. The dipole moment of *N_2 is also visualized. (E) A schematic diagram is provided to depict the distal path and geometry structure (with distances in angstroms) of the corresponding intermediate involved in the reduction of N_2 to NH_3 on W/MXenes. The inset offers a comparison of free energy diagrams of NRR, differentiating between pristine Ti/$Ti_{3-x}C_2O_y$ (depicted in blue) and W single-atom electrocatalysts (depicted in red). Lastly, the distribution of exchange/polarized charges between the adsorbed NNH (F), NNH_2 (G), and NH (H) species, and W single-atom electrocatalysts, indicating multiple instances of chemical bonding between the N atom and O vacancy. The yellow and blue areas represent negative and positive charges, respectively, with isosurface values of 0.005 e Å^{-3}. Reproduced with permission from ref. 97. Copyright 2020 American Chemical Society.

between MXenes and co-catalysts enhances the overall N_2 fixation performance.[95,98]

Overall, the following are the fascinating features of MXenes crucial in the electrocatalytic N_2 fixation:

4.1 Highly active catalysts

MXenes exhibit high surface area, which provides efficient active sites for catalytic reactions. Their 2D structure with transition metal layers allows for efficient interaction with N_2 molecules and promotes their conversion to desired products like NH_3, thus enhancing the efficiency and selectivity of the N_2 fixation process under ambient conditions.[95,98] Their ability to catalyze the conversion of N_2 to NH_3 under ambient conditions is particularly noteworthy, as it offers a more sustainable and cost-effective approach to ammonia synthesis.

4.2 Tunable surface chemistry

MXenes can be easily functionalized due to the availability of the surface termination groups present on their layers. This allows for the modification of their surface chemistry, tailoring it to specific reaction requirements.[99] Besides, this surface functionalization can optimize the electrocatalytic performance of MXenes by enhancing the adsorption and binding affinity of N_2 on the MXene surface, thus promoting the catalytic reduction of N_2 to NH_3.[95,100]

4.3 Electrical conductivity

MXenes have high electrical conductivity, which is advantageous in electrocatalytic reactions.[67] The presence of conductive pathways throughout the MXene structure facilitates the efficient transfer of electrons during the N_2 fixation process. This enables improved charge transfer kinetics and reduces energy losses, leading to enhanced electrocatalytic activity; conductivity of MXenes contributes to their overall performance as efficient catalysts for N_2 fixation.[101,102]

4.4 Stability and durability

Various MXene-based composites exhibit excellent thermal and chemical stability, making them ideally suited for long-term electrocatalytic N_2 fixation. They can withstand the harsh conditions involved in the reaction, such as high temperatures, corrosive environments, and electrochemical cycling. The stability and durability of MXenes ensure their sustained catalytic activity, enabling efficient and continuous N_2 fixation without significant degradation or loss of performance.[103,104] Several factors influence the stability of MXenes to oxidation, including their chemical composition, surface functionalization, and structural characteristics,[105,106] a critical consideration for their successful utilization in practical applications.

MXenes are prone to oxidation and degradation, which can significantly affect their performance over time. So, research efforts ought to focus on enhancing the environmental stability of MXenes, possibly through surface passivation, protective coatings, or the development of more robust MXene composites. Ensuring the long-term stability is particularly important for applications in harsh environments, such as electrochemical reactors and energy storage devices.

4.5 Integration with other materials

MXenes can be combined with other materials to form hybrid structures, offering additional benefits for electrocatalytic N_2 fixation. For instance, MXenes can be integrated with carbon-based materials, such as graphene or carbon nanotubes, to enhance their conductivity and provide a synergistic effect on catalytic performance. The ability to combine MXenes with other materials expands their potential for achieving superior electrocatalytic properties in N_2 fixation.[67,98]

In one study, the potential application of a few-layered $MoSe_2$ on $Ti_3C_2T_x$ MXene was investigated as an efficient catalyst for electrochemical NRR (Fig. 3).[107] The $MoSe_2/Ti_3C_2T_x$ catalysts were synthesized *via* a simple one-step hydrothermal method followed by thermal annealing. The experimental results demonstrated that the catalysts exhibited a noteworthy NH_3 yield rate of 56.96 $\mu g\ h^{-1}\ mg_{cat}^{-1}$ along with the remarkable faradaic efficiency of 14.08%, while maintaining excellent electrochemical stability. It was indicated that the Mo atoms served as active sites for electrochemical NRR, with the distal pathway being the preferred route for NH_3 production on the catalyst.[107] The deployment of this method offered a sustainable procedure for producing NH_3, while reducing the energy need for Haber–Bosch process and decreasing the associated greenhouse gas emissions. The combined usage of these two compounds led to an increase in the stability of the composite, making it suitable for a longer-time practice.

Importantly, without further improvements, MXenes have been found to exhibit insufficient catalytic activity for the electrochemical NRR due to the presence of inactive functional groups, particularly F* and OH*, which cover the active metal sites responsible for N_2 binding.[75,82] In one study, the surface termination of MXene ($Ti_3C_2T_x$) nanosheets was successfully modified to enhance their surface catalytic reactivity for NRR (Fig. 4).[75] This was achieved by eliminating the inactive F/OH terminations to expose more active sites and by introducing iron (Fe) to significantly reduce the surface work function. The optimized catalyst, denoted as MXene/$TiFeO_x$-700, exhibited outstanding faradaic efficiency of 25.44% and high NH_3 yield of formation, surpassing all previously reported MXene-based catalysts for NRR. Findings from this study offered a viable strategy for systematically enhancing the surface reactivity of MXene-based catalysts, by enabling the electrochemical N_2 conversion with high efficiency. The authors worked on improving the catalytic performance of MXenes by reducing the amounts of inactive functional groups and the attachment of the Fe ions. Besides, by optimizing the catalyst, one could attain high efficiency and yield under ambient conditions which represents a step towards more sustainable and environmentally friendly ammonia production methods, that are so crucial for agriculture and industry.[75]

Utilizing first-principle density functional theory (DFT) and *ab initio* molecular dynamic (AIMD) calculations, Fang *et al.*[108] extensively explored the reactivity, specificity, and thermodynamic stability of Fe and Ru single-atom or tetra-nuclear metal clusters supported on MXene (Nb_2C). The MXene was modified with oxygen (fluorine) functional groups, leading to the creation of a remarkable electrocatalyst, denoted as Ru/Nb_2CO_2, for the process of N_2 reduction. The outcomes from this study indicated that the Ru/Nb_2CO_2 catalysts primarily facilitated the electro-reduction of N_2 *via* an enzymatic hybrid mechanism, exhibiting an impressive selectivity of 99.9% and a low ΔG_{PDS} of 0.59 eV. Furthermore, this catalyst demonstrated exceptional stability even at elevated temperatures (227 °C), showcasing its immense potential for the electrocatalytic production of NH_3 with high efficiency.[108] According to these results, introducing new elements, like Fe or Ru, on the structure of MXenes as well as the exceptional selectivity and low energy barriers for the NRR on Ru/Nb_2CO_2 could significantly affect their electrocatalytic properties and enhance their ability for producing $NH_{3.}$ This could lead to more sustainable and economically viable methods for ammonia production, thus reducing reliance on the energy-intensive Haber–Bosch process. While the computational predictions are promising, experimental validation is crucial to confirm the performance and stability of Ru/Nb_2CO_2 under real-world conditions and future research should focus on synthesizing this catalyst and testing it in electrochemical cells to assess its practical viability.

To help the evolution of sustainable ammonia synthesis, a fundamental innovative step is needed, and that is critical analysis of electrocatalytic N_2 fixation using MXenes. To this end, each research step in this process should be analyzed to understand the core strengths and weaknesses of the existing methodologies. For this purpose, various approaches employed in the electrocatalytic reduction of N_2 on MXene surfaces ought to be evaluated with a deeper understanding of their main mechanism of action. In other words, the proposed mechanisms for the N_2 reduction on MXene surfaces are like an interesting puzzle that needs to be fixed with each other using a combination of experimental and computational investigations to realize the full potential of MXenes in N_2 fixation. Therefore, additional studies are needed in this context to address the inconsistencies that persist in different reports to have a clearer understanding about the effect of MXenes and their varied properties on N_2 reduction. Another critical point that ought to be considered is the stabi-

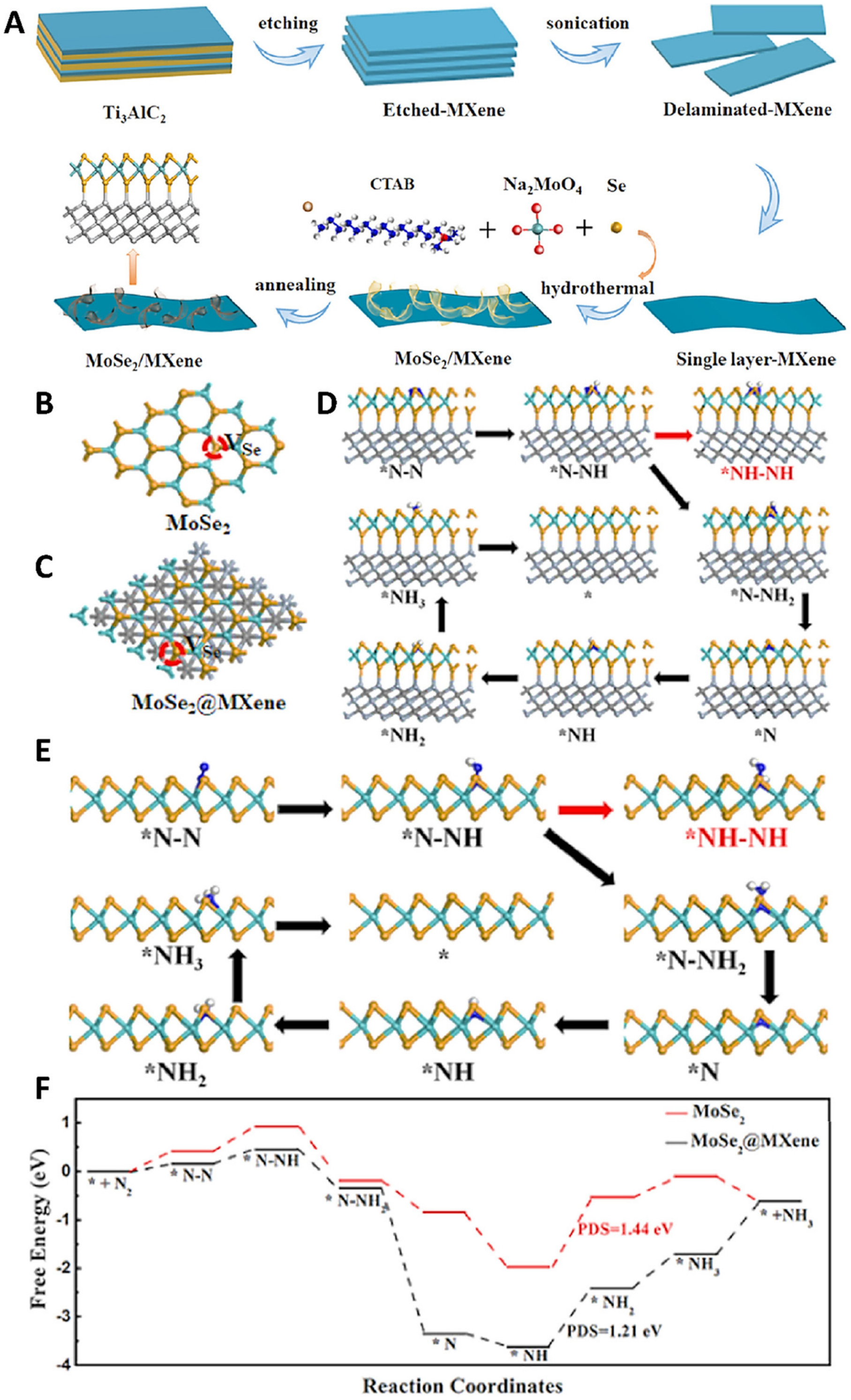


Fig. 3 (A) The preparative process for $MoSe_2$/MXene composites. Optimized structures of (B) $MoSe_2$ and (C) $MoSe_2$/MXene for the electrochemical NRR. The optimized structures of intermediates for the electrochemical NRR on (D) $MoSe_2$/MXene and (E) $MoSe_2$. (F) Free energy diagrams on $MoSe_2$ and $MoSe_2$/MXene along the distal pathway of the electrochemical NRR, respectively (asterisk (*) specifies adsorption site) (brown (Se); iron blue (Mo); gray (Ti); silver-white (C)). CTAB: cetyltrimethylammonium bromide. Reproduced with permission from ref. 107. Copyright 2022 American Chemical Society.

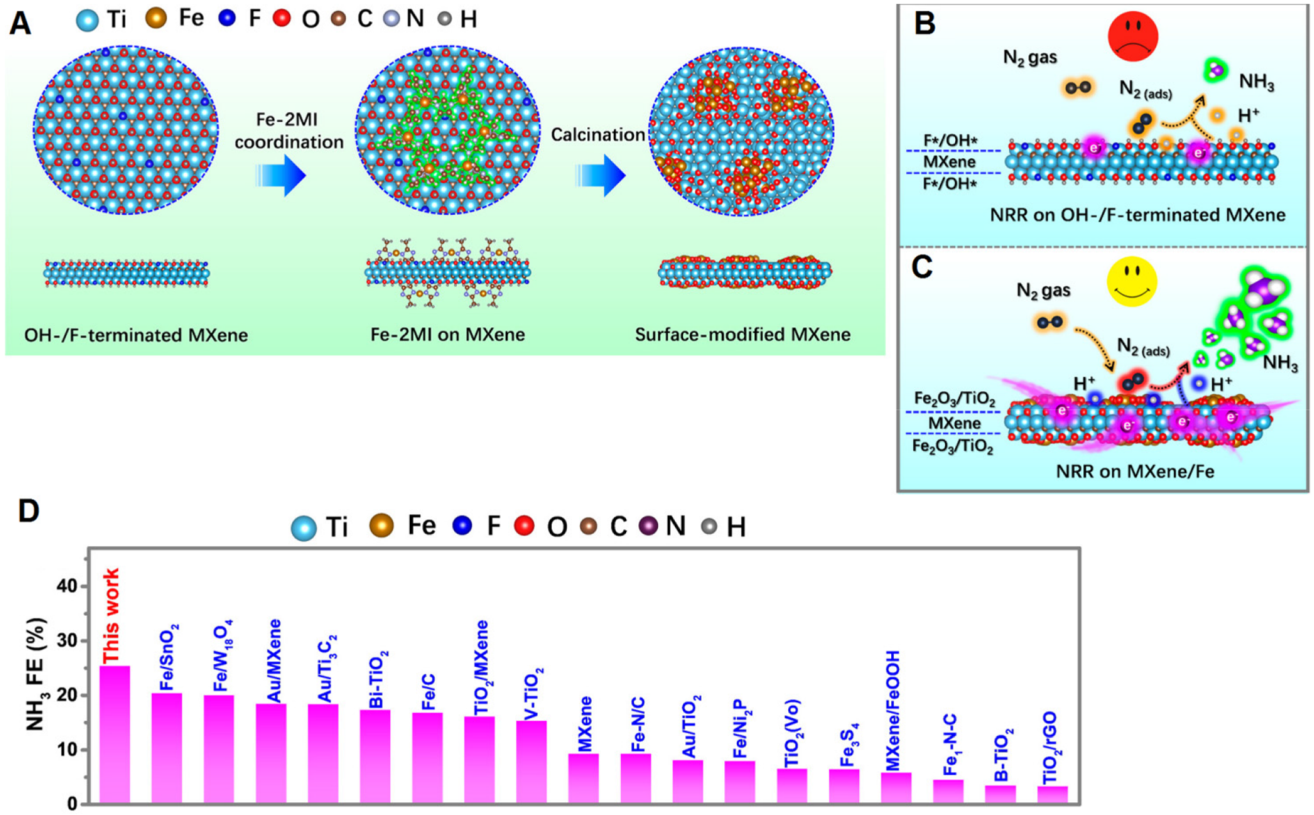


Fig. 4 (A) The preparative process of the surface-modified MXene/$TiFeO_x$ nanosheets. (B and C) The electrochemical reduction of N_2 to NH_3 using pristine MXene and MXene/$TiFeO_x$-700 catalysts. (D) The comparison of faradaic efficiencies of the modified MXene (MXene/$TiFeO_x$-700) with other reported MXene-, Fe-, and Ti-based catalysts. Reproduced with permission from ref. 75. Copyright 2020 American Chemical Society.

lity of MXenes that has direct effect on their practical application in electrocatalytic N_2 fixation. Different protocols have been deployed with this aim but the effectiveness of these strategies in maintaining the catalyst's activity while prolonging its lifespan is a question that needs to be answered through critical evaluation.[109,110]

It worth mentioning that although the integration of MXenes with other materials, such as metals, metal oxides, and carbon-based materials, has shown to enhance their performance through synergistic effects, this interaction is complex and requires careful optimization. The development of hybrid systems with well-defined interfaces and optimal compositions can lead to significant improvements in performance. Research should focus on understanding these interactions and developing strategies to maximize the synergistic effects.

5. Strategies to enhance MXenes' electrocatalytic performance

5.1. Surface modification and functionalization of MXenes

As stated earlier, the surface modification of MXenes is a vital process that enhances their properties and expand their potential applications by altering the surface of MXene materials using various functional groups or nanoparticles, thereby tailoring their surface chemistry and physical properties. The surface modification of MXenes can improve their stability, enhance their conductivity, and increase their affinity towards specific molecules or ions.[67,111,112] This opens up avenues for the deployment of MXenes in electrocatalytic applications, especially electrocatalytic N_2 fixation. Surface modification can enhance the stability of MXenes by protecting them from environmental factors such as moisture or oxidation thus enabling their prolonged usage and improved performance in various applications. For instance, a straightforward silylation reaction was developed to effectively protect MXenes against structural degradation caused by spontaneous oxidation, which enhanced their surface features by adjusting hydrophilicity. This modification improves the stability of MXenes by providing a protective layer against environmental factors such as moisture and oxidation, which is crucial for applications demanding long-term durability.[113]

To evaluate the stability and changes in surface properties, (3-aminopropyl) triethoxysilane-functionalized MXene (APTES-MXene) was selected as the model. Accordingly, the MXene's stability in air decreased by 17.1%, 35.4%, 65.3%, and 95.6% after 1, 3, 6, and 11 days, respectively. In contrast, APTES-MXene only experienced a 20.8% reduction in stability after 11 days.[113] Herein, adjusting the hydrophilicity through surface modification have led to enhance the interaction of MXenes with other substances, that potentially improved catalytic performance of MXenes. Therefore, the application of silylation reactions to protect MXenes from oxidation is a promising approach that can significantly extend their usability. However, the fact that modified MXenes still experience a gradual decrease in stability highlights the need for additional research to develop more robust protective coatings. Additionally, the added complexity and potential cost implications of the modification process should be carefully considered in the development of commercially viable MXene-based products.

The other effect of surface modification is enhancing the operational capability of MXenes in ion adsorption, increase their charge storage capacity, and improve their catalytic activity. By modifying the surface and structure of MXenes, their properties, like electrical conductivity or catalytic activity, can be adjusted to specific requirements thus promoting the usage of customized MXenes in diverse applications.[85] For instance, the spin order of transition metal embedded-MXenes was regulated for enhancing the electrocatalytic N_2 reduction to NH_3.[114]

Wei *et al.*[115] demonstrated the evidence that transitioning from a 2D structure, such as nanosheets, to a 3D nanostructure, like nanoribbons, resulted in a remarkable improvement in N_2 fixation activity due to the creation of exposed Ti–OH sites. This structural modification leads to an increase in active sites available for the reaction, resulting in improved catalytic performance; however, this added complexity could pose challenges for large-scale production and commercialization. Remarkably, a direct correlation has been recognized between the rate of NH_3 formation and the quantity of oxygen present on the surface of Ti_3C_2 MXenes.[115] This finding suggests that the presence of oxygen-containing functional groups, such as Ti–OH, play a crucial role in the catalytic activity of MXenes for N_2 fixation. Controlling the quantity and distribution of these groups on the surface of MXenes can be challenging and may require precise synthesis and modification techniques to fully harness the potential of MXenes in electrocatalytic applications.

Modifying the surface of MXenes enables them to be integrated with other materials, such as polymers or nanoparticles, to create composites with synergistic attributes.[116] This expands the range of applications for MXenes and promotes the development of advanced hybrid materials. Despite the numerous benefits of surface modification, there are still challenges that need to be addressed.[117] The achievement of uniform and controlled surface modification while preserving the intrinsic properties of MXenes remains a significant hurdle. Notably, the selection and design of suitable functional groups or nanoparticles require careful consideration to ensure compatibility and optimal performance. Future research in MXene surface modification ought to focus on the development of efficient and scalable methods that can be easily implemented in large-scale production. Furthermore, a deeper understanding of the interaction between MXenes and functional groups/nanoparticles is needed to guide the design and synthesis of modified MXenes with enhanced properties.[118]

Surface modification of MXenes through the introduction of suitable functional groups or nanoparticles can lead to enhanced catalytic, electronic, and mechanical properties, making them ideally suited for various applications and enabling the customization of these materials. However, achievement to the uniform and controlled surface modification without altering the intrinsic properties of MXenes is a challenging proposition. Inconsistencies in modification can lead to variations in performance, which can be problematic for applications that require precise material properties. Moreover, selection of appropriate functional groups or nanoparticles for surface modification is crucial as the incompatibility between the modifying agents and the MXene surface can result in a poor performance or even degradation of the material. Thus, although surface modification holds great promise for solving the potential of MXenes in various applications, but there are some challenges that ought to be considered while developing such processes.

In an impressive study, an investigation was conducted involving a total of 65 bare and functionalized MXenes.[119] The free energy diagrams for the NRR were analyzed on the basal planes of 55 different M_2XT_x MXenes, where M represents elements such as Ti, V, Zr, Nb, Mo, Ta, and W, while X represents elements C and N. The energy trends were established based on the metal and nonmetal constituents of the MXenes, considering both, the bare and functionalized forms. Through the analysis, the limiting potentials for the NRR were identified. For bare MXenes, the potential limiting reaction step involved the formation of NH_3 from $*NH_2$, while for functionalized MXenes, it was the formation of $*N_2H$. It was discovered that certain MXenes encompassing Mo, W, and V (specifically Mo_2C, Mo_2N, W_2N, W_2NH_2, and V_2N) exhibited suitable theoretical over-potentials for the NRR. However, when the calculated Pourbaix stability diagrams and conducted selectivity analysis were examined, all bare MXenes were found to be unstable under relevant NRR operating conditions.

Among the functionalized MXenes, W_2CH_2, a H-terminated MXene, was identified as the only one possessing all three required properties: a low theoretical overpotential, stability under NRR conditions, and selectivity towards NRR rather than the parasitic hydrogen evolution reaction.[119] The extensive dataset provided by this study allowed for a thorough comparison of various MXene compositions and functionalization, highlighting the versatility of these materials which offer a beneficial guidance for the selection of MXenes for further experimental investigations and appliances in electrocatalytic N_2 fixation; functionalized MXenes displayed better performance in NRR. Moreover, by considering a broader range of MXenes, the variety and tunability of options can be expanded for the NRR.

The recognition of intrinsic active sites and understanding their kinetic processes on electrocatalysts are crucial for the rational design of highly efficient electrochemical N_2 fixation electrocatalysts.[29,98,120] One of the important factors that could affect the efficiency of electrocatalysis is the positioning of active groups. In this context, Wang and colleagues made an important discovery regarding MXene ($Ti_3C_2T_x$) nanosheets when appended to a vertically aligned metal host (Fig. 5).[98] They found that these nanosheets exhibited a high faradaic efficiency of 5.78% for the NRR at an extremely low potential, enabling efficient NH_3 electro-synthesis. The MXene possessed a single-layered structure with a T–Ti–C–Ti–C–Ti–T sandwich configuration. Within this structure, various atomic sites, including C, O, lateral Ti, and middle Ti, are present. They discovered that the middle Ti atom exhibited the highest adsorption energy (E_{ads}) for N_2, measuring at −1.34 eV. This suggested that the NRR activity on the edge planes of MXene, which have exposed middle Ti sites, would be superior to that on the basal planes with terminal O sites. In addition, the calculated E_{ads} for N_2 on the middle Ti sites of the edge planes was higher than that for H_2O (−1.00 eV) and H (−0.93 eV), indicating the preferential adsorption of N_2 on the edge planes. The researchers predicted that the formation of H_2 on the O atoms was endothermic by 0.13 eV, while the first hydrogenation of N_2 on the middle Ti atom was exothermic by −0.13 eV. This suggests that even if the adjacent O atoms on the edge planes were considered as possible sites for H adsorption to produce H_2, the same prediction would hold true.

Indeed, these calculations indicate that, at suitable overpotentials, the NRR is favored over the hydrogen evolution reaction (HER) on the edge planes of MXene. Overall, these findings offer valuable insights into the active sites and mechanisms involved in the NRR deploying MXenes, especially the presence of active functional groups at the edge of MXenes, thus paving the way for developing efficient electrocatalysts for N_2 fixation.[98] However, fabrication of MXene nanosheets with a specific orientation and the precise positioning of active groups may involve complex synthesis processes, which could pose challenges for large-scale production. While the study offers valuable insights into the active sites and underlying mechanisms involved in NRR using MXenes, a comprehensive understanding is still lacking thus highlighting the importance of further explorations to fully elucidate the catalytic processes and optimize the performance of MXene-based electrocatalysts.

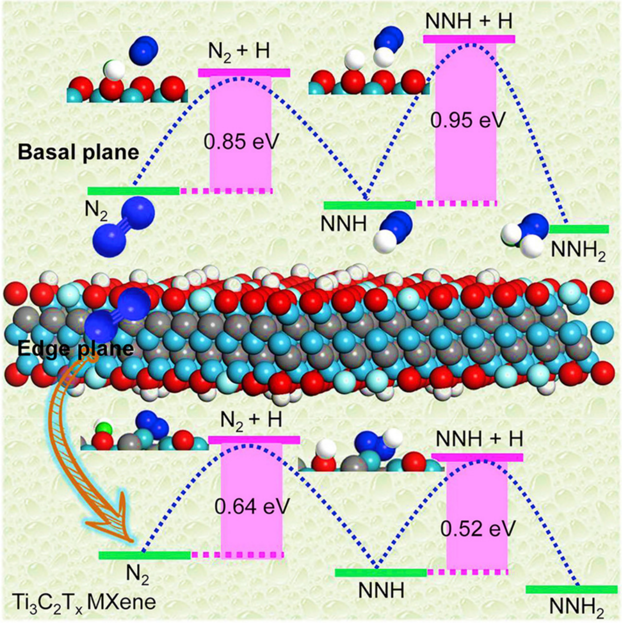


Fig. 5 The structure of MXene ($Ti_3C_2T_x$) and a comparison of the activation barriers on the basal plane and the edge plane. Reproduced with permission from ref. 98 Copyright 2018 Elsevier.

Shi *et al.*[29] developed 3D nitrogen (N)-doped-Ti_V-$Ti_{3-x}C_2T_y$-1.2 MXene for electrochemical NRR wherein they revealed that the Ti^{3+} species served as the intrinsic active sites for electrochemical NRR on the porous N-doped $Ti_{3-x}C_2T_y$ MXene. The electronic state of these active Ti^{3+} species could be adjusted *via* surface atomic engineering techniques such as creating vacancies and doping heteroatoms. The introduction of Ti vacancies enabled the trapping of electrons injected into the anti-bonding orbital of adsorbed N_2, thus facilitating N_2 activation. Besides, the N-dopant species in the MXene not only acted as stable active sites for electrochemical NRR but also promoted the desorption of NH_3 by minimizing the orbital overlap between Ti^{3+} and N_2.[29] The introduction of Ti vacancies and N-doping not only enhanced the electrocatalytic activity, but also offered stable active sites for the reduction of N_2 to ammonia thus providing a high degree of control over the crucial catalytic properties of the MXene that is vital for optimizing the performance of the electrocatalyst.

The innovative approach of deploying surface engineering techniques to enhance the performance of MXenes is promising for the development of efficient electrocatalysts for ammonia synthesis. The tunability of active sites and the facilitated N_2 activation are particularly impressive features that can lead to significant improvements in catalytic efficiency. However, ensuring the uniformity and reproducibility in the material's properties is crucial for its practical application. The durability of the active sites and the structural integrity of the MXene are important factors for its application in industrial processes. Thus, the long-term stability of these materials under electrochemical reaction conditions needs further investigation.

5.2 Alloying and hybridization with other nanomaterials

Alloying and hybridization of MXenes with other nanomaterials is a promising strategy to further enhance their properties and create advanced materials with unique characteristics. These processes involve combining MXenes with different types of nanomaterials, such as nanoparticles, nanowires, or nanosheets, to create composites that exhibit synergistic behavior and improved performance. Such amalgamation can lead to the emergence of synergistic properties, where the combined materials exhibit enhanced performance relative to the individual components. This can include improved electrical conductivity, mechanical strength, or specific functionalities like catalytic activity or chemical stability.[121–123] Moreover, this combination can improve the chemical stability of the composite, rendering it more resistant to degradation under harsh conditions, which is important for extending the lifespan of the material in various appliances.

One popular approach is the incorporation of MXenes into metal or metal oxide nanoparticles[124] which can be achieved through various methods, including wet chemical synthesis, electrochemical deposition, or physical mixing. These MXene–metal/metal oxide composites combine the excellent conductivity and mechanical properties of MXenes with the catalytic or magnetic properties of metal/metal oxide nanoparticles.[124,125] Hybridization of MXenes with other nanomaterials involve the integration of MXenes with carbon-based nanomaterials, such as graphene or carbon nanotubes.[126] For instance, reduced graphene oxide supported MXene based metal oxide ternary composite electrodes were fabricated for non-enzymatic glucose sensor purposes.[127] The combination of MXenes and carbon-based nanomaterials can lead to enhance electrical conductivity, mechanical strength, and improve electrochemical performance in energy storage and conversion devices.[121] This complexation improves the stability of MXenes and makes them a good candidate for applications in energy storage and conversion devices, where efficient electron transfer is indispensable for optimal performance.

A precise control over the synthesis conditions is needed for large-scale production and reproducibility and challenges associated with the synthesis process and ensuring uniform dispersion of the components need to be addressed to fully realize the potential of these materials. Additional explorations are also warranted to understand the fundamental mechanisms governing the interaction between MXenes and different nanomaterials, enabling precise control over their properties and functionalities. Overall, the development of MXene-based hybrid materials holds great promise for advancing the field of nanomaterials and their applications in technology.

5.3 Structural engineering of MXenes for improved catalytic performance

Structural engineering of MXenes is a crucial strategy for enhancing their catalytic performance and expanding their potential applications.[128] This approach involves modifying the structural aspects of MXenes, such as their composition, morphology, layer stacking, and interlayer spacing, to optimize their properties and functionalities.

One aspect of structural engineering is the selection and synthesis of MXene precursors.[129,130] By carefully choosing the precursor materials and processing conditions, the composition and morphology of MXenes can be adjusted to achieve desired properties.[131] This includes controlling the type and number of transition metals, as well as the thickness and crystallinity of the MXene layers.

Another important aspect is the manipulation of the interlayer spacing in MXenes. This can be achieved through various methods, such as intercalation of molecules or ions, introduction of functional groups, or incorporation of guest species between the MXene layers.[132] Modifying the interlayer spacing can significantly influence the electrochemical performance, ion diffusion kinetics, and mechanical properties of MXenes.

The engineering of MXene morphology is also crucial for improving their performance.[133] Proper control of the shape, size, and surface area of MXene particles or films is essential. By optimizing the morphology, the specific surface area and accessibility of active sites can be maximized, leading to the enhanced catalytic activity, charge storage capacity, faster ion diffusion, and prolonged cycling stability.[128,130,134]

In addition, structural engineering allows for the tailoring of MXene materials with desired mechanical properties. By controlling the layer stacking, thickness, and interlayer interactions, the mechanical strength, flexibility, and resilience of MXenes can be optimized for specific applications, including flexible electronics, sensors, and structural materials.[134,135]

Through structural engineering, MXenes can be modified to exhibit additional functionalities. For instance, introducing specific functional groups or nanoparticles onto the MXene surface can impart catalytic activity, magnetic properties, or selectivity towards certain molecules. This expands the potential applications of MXenes in fields like catalysis, sensing, biomedical engineering, electronics, energy storage, and environmental remediation.[109,136]

Structural engineering can also enhance the stability and durability of MXenes and their derivatives, making them more resistant to environmental factors (*e.g.*, oxidation or moisture) to ensure prolonged usage and reliability in various applications, including energy storage devices and corrosion-resistant coatings.[137]

Overall, MXenes exhibited significant potential as electrocatalysts owing to their distinctive characteristics, like exceptional conductivity and adjustable surface terminations. Scientists have employed termination modification and heteroatom integration to enhance the chemical and physical attributes of MXene-based catalysts for diverse electrocatalysis processes, encompassing hydrogen evolution, oxygen evolution/reduction, carbon dioxide reduction, and NRRs.[67,138]

Despite the significant progress in structural engineering of MXenes, there are still challenges that need to be addressed. Achieving precise control over the composition, morphology and interlayer spacing of MXenes remains a problem, particularly for large-scale production. Furthermore, understanding the structure–property relationships at the atomic and nanoscale is essential for guiding the design and synthesis of tailored MXene materials.

Future explorations ought to focus on developing scalable and reproducible methods for structural engineering of MXenes. This includes the exploration of new synthesis techniques, characterization methods, and computational modeling to unravel the underlying mechanisms and optimize the performance of MXene materials.[139]

Structural engineering represents a powerful strategy for unlocking the full potential of MXenes and expanding their application horizons. The ability to tailor MXenes' properties through precise control over their structural aspects is incredibly promising for developing high-performance materials tailored for specific needs. However, the challenges associated with the complexity of synthesis and the need to balance the enhancements among various properties must be addressed.

Advances in synthesis techniques and a deeper understanding of MXene structure–property relationships will be crucial for overcoming these challenges and fully leveraging the advantages of structural engineering. Ultimately, the continued exploration and optimization of MXenes through structural engineering hold great promise for a wide range of technological applications, thus underscoring the importance of interdisciplinary research in this field.

The precise control over the structure and composition of MXenes remains a significant challenge. Achieving consistent layer thickness, interlayer spacing, and surface functionalization is critical for optimizing their properties for specific applications. While progress has been made in understanding how to manipulate these parameters, the reproducibility of these modifications at a large scale is still problematic. Future research should focus on developing more reliable and scalable methods for the structural engineering of MXenes to ensure uniformity and consistency in their properties.

5.4 Interface engineering for enhanced N_2 fixation efficiency

Interface engineering is a promising tactic for enhancing the efficiency of N_2 fixation, which is a crucial process for converting atmospheric nitrogen into more usable forms for various applications, including agriculture and chemical synthesis. Indeed, interface engineering can enhance the catalytic activity of N_2 fixation catalysts by optimizing the interfaces between the catalyst and reactants. This includes improving N_2 adsorption, promoting reactant activation, and facilitating the reaction pathways, leading to the higher conversion rates and enhanced efficiency ensuring that the desired products are obtained with minimal side reactions. This is particularly important in chemical synthesis, where the purity of the final product is crucial.[140] In other words, this strategy involves modifying the interfaces between catalysts and reactants to optimize the catalytic activity, selectivity, and overall performance of N_2 fixation process.[140] For instance, interface engineering of MoS_2/C_3N_4 heterostructures was performed for promoting electrocatalytic N_2 fixation, emphasizing the effectiveness of this method in designing powerful catalysts. In here, the NRR activity of the heterostructure was improved by transporting interfacial charge from C_3N_4 to MoS_2 through enhancing the stabilization of $^*N_2H$ (intermediate) on the Mo edge as well as reducing the reaction energy barrier. The MoS_2/C_3N_4 heterostructure demonstrated effective suppression of the competing hydrogen evolution reaction (HER) that was confirmed by the favorable adsorption free energy of *H species on S edge sites of MoS_2, which protects the NRR-active Mo edge sites from HER, leading to a high faradaic efficiency for NH_3 production. The fabricated formulation was a stable active catalyst used for the electrochemical NRR that was benefited from the presence of both of C_3N_4 to MoS_2.[141]

One important aspect of interface engineering is the design and synthesis of catalyst materials with tailored interfaces, which include the optimization of the surface composition, morphology, and electronic structure of the catalysts to facilitate N_2 activation and enhance the adsorption and activation of reactant species. In this context, the activity of transition metal carbide-based electrocatalysts heavily relies on their surface and interfacial characteristics[142] which could be engineered to achieve better control over the selectivity of the N_2 fixation process. This comprises directing the reaction towards desired products and minimizing the unwanted side reactions. By controlling the interfaces, the reactivity of the catalysts can be fine-tuned to achieve higher N_2 fixation efficiency.[143,144]

Interface engineering enables the design of catalysts with tailored selectivity, making them more suitable for specific applications[145,146] besides enhancing the stability and durability of catalyst materials for N_2 fixation. By optimizing the interfaces, catalyst deactivation mechanisms can be mitigated, leading to prolonged catalyst lifetimes and consistent performance over extended reaction periods. Optimizing the interfaces can improve the energy efficiency of the N_2 fixation process by reducing the energy requirements for reactant activation and promoting more efficient reaction pathways.[142,146] This has implications for sustainable nitrogen-based chemical synthesis and fertilizer production.

Sun *et al.*[147] conducted a study on the N_2 capture capability of various MXenes, specifically d^2 (M = Ti, Zr, and Hf), d^3 (M = V, Nb, and Ta), and d^4 (M = Cr and Mo). The researchers focused on transition metal carbides materials that displayed a strong affinity for N_2 capture, as these materials are crucial for electrochemical conversion into ammonia. The calculations revealed that the bonding energy between d^2 MXenes and CO_2 was significantly higher compared to N_2 and H_2O. Interestingly, the chemical adsorption capacity of d^3 and d^4 MXenes for N_2 exceeded that of CO_2 and H_2O. In other words, d^3 and d^4 MXenes displayed a favorable preference for N_2, making them suitable for electrocatalytic NRR under normal environmental conditions.[147] Hence, interface engineering is a powerful strategy for enhancing the performance of catalysts for N_2 fixation. The ability to tailor selectivity, improve stability, and increase energy efficiency makes this approach highly attractive for various applications, especially nitrogen-based chemical synthesis, and fertilizer production. The important point that ought to be considered in the development of these materials for practical applications is the complexity in designing interface-engineered catalysts and the potential trade-offs between various properties.

Li *et al.*[148] proposed the potential use of H-terminated molybdenum carbides as catalysts for electrocatalytic N_2 reduction. They introduced the concept of doping highly electronegative atoms at specific sites to create non-metal terminated carbides with customized N_2 adsorption energy, which is ideal for NH_3 generation. Through DFT calculations, it was confirmed that the interaction between Mo sites and N_2 molecules was weakened on the H-terminated $Mo_2C(100)$ surface, leading to enhanced NH_3 release during the NRR process.[148] The employed doping strategy enabled the customization of N_2 adsorption energy on the catalyst surface which is crucial for optimizing the catalyst's performance in NH_3 generation, as it ensures that N_2 molecules are adsorbed with the precise strength for efficient reduction. Besides, it revealed enhanced NH_3 release that is advantageous for attaining higher yields of ammonia and opens new possibilities for exploring alternative catalyst materials with customized properties. Here, the complexity of doping process and the stability, that is required for long-term usage, are two main concerns that should be considered during the preparation process.

While interface engineering shows great potential for enhancing N_2 fixation efficiency, there are several inadequacies that need to be addressed. Understanding the complex interplay between catalyst interfaces, reaction mechanisms, and reactant species is crucial for designing effective interface engineering strategies. The development of advanced characterization techniques and computational modeling approaches can aid in unraveling these complexities.[135,149–151]

Future investigations ought to focus on developing scalable and cost-effective methods for synthesizing catalysis materials with tailored interfaces. Exploration of new catalyst compositions, novel interface engineering techniques, and innovative reactor designs holds promise for further improving N_2 fixation efficiency. Notably, efforts ought to emphasize the optimization of the durability and long-term stability of catalyst materials under realistic reaction conditions.

5.5 Computational modeling and design of MXenes

Computational modeling and design play a crucial role in understanding and optimizing the properties of MXenes for specific applications and is a powerful technique that uses mathematical and computational methods to simulate and predict the behavior and properties of materials.[152–154] Recently, Zhan *et al.*[150] deliberated on the progress of computational work in the theoretical design of new MXene structures in the context of energy-related applications, accentuating the achievements and possibilities within this domain.[150] Computational methods allow for the exploration of a wide range of structures and compositions that may not be easily accessible through experimental means.

Another study showcased the notion of fine-tuning MXene's electronic characteristics *via* functionalization in the high-throughput design of functional-engineered MXene transistors, featuring low-resistance contacts through computational methods.[155] This is a cost-effective approach for exploring the vast design space of MXenes and allows for the screening of a large number of materials and configurations without the need for expensive and time-consuming experiments. Importantly, while the computational modeling is powerful, its accuracy depends on the underlying theoretical models and parameters deployed and validation of computational predictions through experimental data is essential to ensure reliability.

A systematic investigation has been performed on various MXenes, including 3d, 4d, and 5d-transition metals in their M_2C form, to assess their potential as catalysts for the NRR.[156] It was revealed that $4d^4$-Mo_2C exhibited the lowest free-energy barrier (ΔG) of 0.46 eV among the synthesized M_2C MXenes available to date. However, it is worth noting that two hypothetical MXenes, namely $3d^5$-Mn_2C and $3d^6$-Fe_2C, demonstrated even lower ΔG values of 0.28 and 0.23 eV, respectively, compared to the state-of-the-art $4d^4$-Mo_2C thereby suggesting that Mn_2C and Fe_2C might potentially serve as more efficient catalysts for NRR. In addition, a strong correlation could be found between the d-electron arrangement in the occupied and empty spin-split d-orbitals and the N_2 capture strength, which is a crucial factor in the potential-limiting step. The exceptional performance of Mn_2C and Fe_2C in NRR could be due to their suitable half-filled $3d^5$ and $3d^6$ electron arrangements, respectively. Specifically, the adsorption of N_2 on Mn_2C involved the donation of 1σ electrons to the empty spin-down 3d orbitals of Mn which weakened the N_2 adsorption strength and consequently lowered the energy barrier for the potential-limiting step of hydrogenation. The findings offered valuable assistance in designing novel MXene-based electrocatalysts for N_2 fixation with high efficiency,[156] especially the correlation found between the d-electron arrangement in the occupied and empty spin-split d-orbitals. Furthermore, the N_2 capture strength provides valuable insights into the mechanism of N_2 fixation that can guide the design of novel MXene-based electrocatalysts with optimized performance. Indeed, the systematic investigation conducted on various MXenes for their potential as catalysts for NRR is an admirable effort in advancing our understanding of these materials. The identification of Mn_2C and Fe_2C as potential candidates with lower free-energy barriers for NRR is particularly exciting, as it opens up new possibilities for the development of efficient electrocatalysts for ammonia synthesis. However, the challenges associated with the synthesis and stability of these materials need to be addressed to realize their full potential in addition to the experimental validation of their catalytic performance and suitability for NRR.

In the context of MXenes, computational modeling involves the use of simulation tools in several ways to study their atomic and electronic structures, as well as their mechanical, thermal, and electrical properties.[150,157,158] Firstly, it helps in the prediction and understanding of MXene structures and their stability under different conditions. By simulating the atomic structures and performing energy calculations, the identification of the most stable MXene configurations and exploration of their properties can be accomplished thus making it an essential tool for designing novel MXenes with tailored properties,[129] DFT being a widely used computational method for modeling MXenes. Molecular dynamics simulations are also employed to study the mechanical and thermal behavior of MXenes under different conditions. Machine learning algorithms are being increasingly deployed to accelerate the discovery and design of new MXene materials by predicting their properties based on existing data.[67,159]

Luo *et al.*[160] conducted an extensive study using DFT methods to analyze the mechanical properties of functionalized MXenes. They performed calculations on various MXene structures to examine the influence of transition metals and surface functional groups on their characteristics, including elastic constants, free energy, and work function. With the exception of certain MXenes bearing O-termination groups, the majority of their material models were found to be dynamically stable. The study concluded that Young's moduli for the investigated MXenes ranged from 150 to 400 N m^{-1}, suggesting that functionalized MXenes generally exhibit enhanced structural stability.[160] The use of DFT methods to examine the influence of transition metals and surface functional groups on their properties offers valuable insights that can guide the design and development of MXene materials. The wide range of Young's moduli reported in the study highlights the versatility of functionalized MXenes and their potential for customization to meet specific applications. However, the constraints associated with DFT calculations and the exclusion of O-terminated MXenes from dynamic stability suggest that there is still much to learn about these materials and consequently, further research is warranted to comprehend these limitations and to fully unlock the potential of functionalized MXenes in various applications.

Shao *et al.*[161] introduced a group of catalysts based on MXenes, comprising M_2X compounds (where M represents Mo, Ta, Ti, and W, and X stands for C and N) which revealed immense potential for N_2 fixation, as demonstrated by DFT calculations; catalytic performance of MXenes being closely linked to the energy of each reaction step. Specifically, it was observed that more exothermic steps resulted in higher catalytic activity during N_2 fixation wherein the energy of N_2 fixation was significantly influenced by charge transfer dynamics: (i) when N atoms undergo electron gain during a step, the reactions develop exothermic with larger reaction energy. (ii) Conversely, if N atoms experience electron loss, the reactions tend to be endothermic. This study demonstrated the exceptional activity of Mo_2C and W_2C in N_2 fixation due to their exothermic reactions and substantial charge transfer[161] and offered a clear guideline for evaluating and optimizing MXene catalysts based on their reaction energetics. According to the outcomes, understanding how electron gain or loss during reaction steps affects the exothermic or endothermic nature of the reactions is essential for designing more efficient catalysts. In other words, identification of a clear link between catalytic performance and reaction energy, as well as the role of charge transfer dynamics, provides valuable guidelines for the design and optimization of MXene catalysts. However, the complexity of charge transfer dynamics and the need for further validation of the findings across other types of catalysts suggest that there is still much to be explored in this area. Continued research on MXene catalysts, including experimental validation and exploration of additional MXene compositions, will be crucial for fully harnessing their potential in catalysis.

Despite its numerous benefits, computational modeling of MXenes also faces challenges. The accurate description of van der Waals interactions, which play a significant role in the stability and properties of MXenes, is one such limitation. In addition, the scale and complexity of MXene systems require advanced computational resources and efficient algorithms to perform simulations in a reasonable timeframe.[149,152,155,162]

Overall, computational modeling can be considered as a valuable tool that complements experimental research in MXene design, providing insights into the atomic-level behavior of MXenes as well as helping researchers to interpret experimental results and guide additional explorations. Notably, computational modeling can direct the synthesis and fabrication processes by predicting the stability of different MXene structures, thereby saving time and resources in experimental trials.

6. Challenges

N_2 fixation is a critical step in the nitrogen cycle and has significant implications for agriculture and sustainability. While MXenes have shown promise in various applications, there are still several limitations and prospects that need to be considered for their effective employment in N_2 fixation. One of the primary challenges is to develop MXene-based electrocatalysts with high activity and selectivity for N_2 fixation. While MXenes possess unique properties such as high conductivity and abundant active sites, further optimization is required to enhance their catalytic performance and render them more efficient in driving the N_2 fixation reaction. Designing MXenes with specific compositions and functional groups can enhance their electrocatalytic activity for N_2 fixation. In addition, the modification of the surface chemistry of MXenes by introducing dopants or functional groups can promote the adsorption and activation of nitrogen molecules, facilitating the N_2 reduction process.[96,98] For instance, the boron-doped Mo_2CO_2 and W_2CO_2 MXene structures exhibited excellent catalytic performance as well as high selectivity with limiting potentials of −0.20 and −0.24 V, respectively.[163]

The integration of MXenes with suitable co-catalysts can further enhance their N_2 fixation activity. For instance, the combination of MXenes with transition metal nanoparticles or molecular catalysts can promote electron transfer and improve the overall catalytic efficiency. Coating MXene surfaces with conformal layers of co-catalysts can improve stability and selectivity. Studies have indicated that the catalytic performance of transition metal single atoms can be assessed by examining their adsorption behavior on MXenes.[96]

Investigations on various MXenes with nitrogen and transition metal layers have demonstrated a favorable ability for initial N_2 fixation and dissociation, with facilitated N_2 adsorption.[164] These results underscore the potential of MXenes as efficient electrocatalysts for N2 fixation, highlighting the importance of optimizing their composition and surface properties.

While MXenes have shown promising catalytic performance in various reactions, including N_2 fixation, the underlying mechanisms driving their activity are not fully understood. Detailed mechanistic studies are essential to uncover the exact roles of different surface terminations, defects, and dopants in enhancing catalytic performance. Advanced characterization techniques and computational modeling can provide deeper insights into these mechanisms, guiding the design of more effective MXene-based catalysts.

MXenes are susceptible to degradation under harsh reaction conditions, such as high temperatures and corrosive environments. Thus, enhancing the stability of MXenes and preventing their structural degradation during the N_2 fixation process is crucial for long-term and sustainable catalytic performance. Strategies such as surface passivation, protective coatings, and morphological control can enhance the stability of MXenes against corrosion, dissolution, and surface reconstruction, enabling sustained electrocatalytic performance.[106,110,165,166] The delineation of the underlying mechanisms behind the oxidative degradation in MXene suspensions is crucial for advancing their practical applications. The delay in oxidative decomposition of MXenes and their derivatives can be effectively attained by carefully controlling a range of pre- and post-fabrication criteria. These include factors such as the quality of the parent MAX phase, the specific type and concentration of acid etchants deployed during chemical etching, the application of ultrasonication, and the storage environment. Parameters related to the storage environment encompass aspects such as the type of storage media, temperature, pH, and the concentration of the aqueous dispersions. By carefully managing these parameters, it is possible to significantly enhance the stability and longevity of MXene suspensions.[106,165]

Understanding the kinetics and reaction mechanism of N_2 fixation on MXene catalysts is essential for the rational design of the catalysts.[167] The complex nature of the N_2 fixation reaction requires a thorough investigation of the reaction pathways, intermediates, and rate-determining steps. Deepening our understanding of the electrochemical reaction mechanisms involved in N_2 fixation on MXene catalysts is crucial for improving their performance. Advanced characterization techniques, such as *in situ* spectroscopy and *operando* measurements, can provide insights into the active intermediates and reaction kinetics, enabling targeted improvements in catalytic activity and selectivity. Innovations in characterization techniques can also offer detailed insights into the structural and electronic properties of MXenes, enabling the precise analysis of MXene-based catalysts and the correlation of their properties with electrocatalytic performance.[98,112] In addition, computational modeling and experimental studies can afford insights into the underlying mechanisms and guide the development of more efficient MXene catalysts.[96]

Gouveia *et al.*[168] employed computational methods to investigate the potential of MXene materials as catalysts for N_2 dissociation using DFT with dispersion corrections. Their findings demonstrated that MXenes exhibited exothermic adsorption of N_2, with substantial adsorption energies ranging from −1.11 to −3.45 eV, leading to ∼20% elongation of the N_2 bond length. This significantly facilitated the dissociation of N_2, with energy barriers below 1 eV and as low as 0.28 eV in the case of W_2N, which exhibited the most favorable conditions. Furthermore, utilizing micro-kinetic simulations, it has been determined that the initial hydrogenation of adsorbed atomic nitrogen was feasible at low pressures and moderate temperatures. The results further support the potential of MXenes for effective nitrogen dissociation and suggest the possibility of combining them as co-catalysts with Ru nanoparticles to enhance the efficiency of NH_3 production.[168] By combining computational modeling and experimental validation, researchers can gain insights into the structure–activity relationships of MXene catalysts. This knowledge can guide the rational design of MXenes with optimized active sites, electronic properties, and surface structures, thereby enhancing their electrocatalytic performance for N_2 fixation.

N_2 fixation involves multiple reaction pathways, leading to the formation of various nitrogen-containing products. The achievement of high selectivity towards NH_3 production as well as the reduction of the formation of undesired byproducts is a significant task. Developing MXene-based electrocatalysts that can precisely control the reaction pathways and optimize the selectivity of N_2 fixation is an area of active research.[95,98] For instance, the adjustment of both high activity and selectivity in electrochemical N_2 fixation has been explored *via* the utilization of single atoms supported on monolayers of Ti_2CO_2 and Mo_2CO_2 MXene.[167] Scaling up the production of MXenes and developing cost-effective manufacturing techniques are critical for their widespread adoption in electrocatalytic N_2 fixation. Large-scale economical synthesis of MXenes with controlled morphology and composition, are essential for their practical implementation in industrial-scale N_2 fixation systems.[129,156] Despite the promising laboratory-scale results, the scalability of MXene production remains a major hurdle. Cost-effective and scalable fabrication processes are essential for the commercial viability of MXenes. Collaboration between academia and industry is necessary to bridge the gap between research and commercial application. Developing standardized protocols for MXene synthesis and processing will be crucial for their widespread adoption.

MXenes are typically used in combination with other materials or catalysts to enhance their performance in N_2 fixation. The hurdle lies in achieving efficient integration and synergistic interactions between MXenes and other components, like transition metal catalysts or supports, to maximize the overall catalytic activity and stability.[95] For instance, a recent study has provided evidence of the synergistic coupling of MXenes ($Ti_3C_2T_x$) with sulfur-deficient Bi_2S_3, to enhance the electrocatalytic N_2 reduction process which offers promising opportunities for further improving the efficiency of MXene-based catalysts.[169]

7. Emerging trends and opportunities

Emerging trends and opportunities in MXenes for electrocatalytic N_2 fixation are opening up exciting possibilities for advancing this critical process. MXenes can serve as excellent platforms for developing single-atom catalysts for electrocatalytic N_2 fixation. By dispersing metal atoms on MXene surfaces, single-atom catalysts can exhibit enhanced catalytic activity and selectivity due to their unique electronic and geometric properties; myriad of surface-functional groups and vacancy defects found on MXenes serve as optimal anchoring sites for individual metal atoms.[170–172] Bai *et al.*[170] have comprehensively reviewed the strategies of anchoring isolated metal atoms onto MXenes and applications of MXene-based single-atom catalysts. In one study, the single-atomic ruthenium modified Mo_2CT_X MXene nanosheets was developed as a highly efficient electrocatalyst for N_2 fixation under ambient conditions.[86] The catalyst exhibited an impressive faradaic efficiency of 25.77% and a substantial ammonia yield rate of 40.57 μg h^{-1} mg^{-1} when operated at −0.3 V compared to the reversible hydrogen electrode in a 0.5 m K_2SO_4 solution. Through *operando* X-ray absorption spectroscopy and DFT calculations, it was discovered that the presence of single-atomic Ru anchored on MXene nanosheets played a crucial role as electron back-donation centers for N_2 activation. This not only enhanced the N_2 adsorption and activation behavior of the catalyst but also significantly lowered the thermodynamic energy barrier of the initial hydrogenation step.[86]

Introducing heteroatoms, such as nitrogen or phosphorus, into MXene structures can modify their electronic properties and enhance their catalytic performance. Heteroatom-doped MXenes can improve the charge transfer kinetics and enhanced binding affinity towards nitrogen molecules, thereby facilitating the electrochemical reduction of N_2.[173] For instance, the inclusion of nitrogen in $Ti_3C_2T_x$ has been observed to result in a decrease in charge transfer resistance and an overall improvement in electrochemical performance which can be attributed to the enhanced charge transfer facilitated by the nitrogen doping process.[174] Likewise, the introduction of nitrogen atoms into titanium carbide sheets has also demonstrated an enhancement in electrochemical performance, due to the incorporation of heteroatom nitrogen.[175] Moreover, the combination of MXenes with other 2D materials or transition metal nanoparticles can create ternary or multicomponent catalytic systems with synergistic effects[176] and the ensued hybrid structures can offer enhanced electrocatalytic activity, stability, and selectivity for N_2 fixation. Thus, further exploration of the integration of MXenes with other materials opens up new opportunities for improved catalytic performance. Surface modifications, such as functionalization or coating with protective layers, can improve charge transfer efficiency, prevent side reactions, and enhance overall stability during N_2 fixation.[67,177]

In this context, development of advanced testing techniques and protocols for the evaluation of MXene catalysts in N_2 fixation is crucial for accurate performance assessment. Techniques such as *operando* spectroscopy, *in situ* electrochemistry, and high-throughput screening methods can offer real-time insights into the catalytic processes, reaction intermediates, and reaction kinetics, thus enabling more precise catalyst design.[67,95] Moreover, computational methods, including DFT calculations and machine learning algorithms, offer opportunities for accelerating the discovery and design of MXene catalysts with desirable properties for N_2 fixation.[178] These techniques can predict the performance of MXenes, guide experimental synthesis, and explore vast compositional and structural spaces for optimal catalyst design.[150] For instance, Du *et al.*[179] developed a simple tactic for preparing Ni nanoparticles supported on MXene ($V_4C_3T_x$) as a highly efficient electrocatalyst for NRR. Impressively, the nanocomposite demonstrated an NH_3 formation rate of 21.29 μg h^{-1} $mg_{cat}{}^{-1}$ at 0.2 mA cm^{-2}. This NRR performance was significantly higher compared to recently reported MXene derivatives and even comparable to noble-metal-based electrocatalysts. Through various characterization techniques and DFT simulations, it has been suggested that the enhanced NRR performance could be attributed to a synergistic NRR pathway involving Ni sites in the nanoparticles and the surface oxygen vacancy of MXene.[179]

As MXene-based electrocatalysts mature, efforts towards industrial-scale synthesis, scalable fabrication processes, and cost-effective manufacturing become increasingly important.[180] Electrochemical N_2 fixation using MXene-based catalysts offers a sustainable and energy-efficient approach to produce ammonia, reducing the dependence on traditional Haber–Bosch processes that require high temperatures and pressures. The selectivity, coupled with their high catalytic efficiency, makes MXenes attractive for industrial-scale electrocatalytic N_2 fixation, where maximizing product yield and minimizing energy consumption are crucial.[95,180] MXenes can be integrated into existing electrochemical setups, such as electrolyzers or flow cells, for efficient N_2 fixation. This compatibility allows for easier adoption and integration of MXenes into industrial processes, thus minimizing the need for significant infrastructure modifications.[67,134]

Overall, collaborations amongst academia, industry, and research institutions are crucial for bridging the gap between laboratory-scale research and commercialization. The partnerships with industry leaders in the fields of catalysis, agriculture, and chemical production can facilitate the development, scale-up, and commercialization of MXene-based electrocatalysts for N_2 fixation. It is worth mentioning that the environmental and economic impacts of MXene production and application need thorough evaluation. While MXenes offer potential benefits, such as reduced energy consumption and lower greenhouse gas emissions in catalytic processes, their overall lifecycle impact must be assessed. Sustainable production methods, recycling strategies, and the economic feasibility of large-scale MXene applications should be key considerations in future research.

8. Conclusion

In recent years, there has been growing interest in finding efficient and sustainable methods for N_2 fixation, as this process is essential for the production of fertilizers and other nitrogen-based compounds. One promising field of research is the utilization of MXenes and their derivatives as electrocatalysts for N_2 fixation due to their unique attributes like good electrical conductivity, high surface area, hydrophilicity, and tunable surface chemistry. One of the key challenges in N_2 fixation is the high activation energy required to break the strong triple bond of N_2. MXenes, with their abundant active sites and strong metal–carbon bonds, offer a favorable environment for nitrogen adsorption and activation. The presence of transition metals in the structure of MXenes further enhances their catalytic performance by facilitating the electron transfer process. Moreover, MXenes can be easily modified with different groups, such as hydroxyl, amino, or transition metal complexes to tune their surface chemistry and improve the selectivity and efficiency of the catalytic process. This versatility allows for tailoring MXenes to specific N_2 fixation reactions and optimizing their performance. The inherent robustness of MXenes, combined with their high catalytic activity, renders those promising candidates for practical implementation in electrocatalytic N_2 fixation systems. However, despite the promising potential of MXenes, there are still some challenges that need to be addressed. In this context, computational modeling may play a vital role in the design and optimization of MXenes by providing insights into their atomic and electronic structures, as well as their properties. It complements experimental research and enables researchers to explore a wide range of MXene compositions and structures, leading to the development of novel MXenes with tailored properties for various applications. Besides, further studies are required in this context to fully expand their potential that could introduce new means for practical appliances in the field of electrocatalytic N_2 fixation, and the transition towards greener and more efficient chemical processes.

Author contributions

Siavash Iravani: supervision, conceptualization, writing – review & editing; Atefeh Zarepour: writing – review & editing; Arezoo Khosravi: writing – review & editing; Rajender S. Varma: review & editing; Ali Zarrabi: writing – review & editing.

Conflicts of interest

The author(s) declare no competing interest.

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