Review Article

Advances in Two-Dimensional MXenes for Nitrogen Electrocatalytic Reduction to Ammonia

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As an important chemical raw material, ammonia is mainly produced by the traditional Haber-Bosch process, which has certain limitations such as high energy consumption, high safety responsibility, and severe pollution, thereby having negative impacts on ecosystem. The synthesis of ammonia from dinitrogen at ambient temperature and pressure is one of the most attractive topics in the field of chemistry. As a new two-dimensional nanomaterial, MXene has excellent electrochemical properties and is a potential catalytic material for electrocatalytic nitrogen fixation. In this review, we firstly introduce the crystal, electronic structures of two-dimensional MXenes and summarize the synthesis methods, N2 reduction, and simulation computation, as well as have insight into the challenges of MXenes, which shed light on the development of highly efficient MXene-based electrocatalysts in the reduction of N2 to ammonia.

1. Introduction

The depletion of fossil fuels and pollution of environment have motivated us to develop clean and sustainable energy storage and conversion technologies and devices [1]. Ammonia (NH3) is a kind of important energy storage intermediate and carbon-free energy carrier, as well as significant raw material for the production of chemical products such as urea and nitric acid. Currently, the global production of NH3 is about 150 million tons per year, and the demand for NH3 is increasing with the rapid growth of the world population. Considering the nitrogen cycle in the environment and 78% of nitrogen (N2) in the air, researchers are interested in the conversion process from N2 to NH3. However, with stable triple N≡N bonds and lack of dipole, N2 molecules are difficult to be activated, resulting in that most chemical reactions cannot be conducted directly. Industrial NH3 production is still dominated by the Haber-Bosch process developed in over 100 years ago [2]. This process is carried out at high temperature (500°C) and high pressure (200-300 atm) using iron or ruthenium-based materials as catalysts and high-purity nitrogen (N2) and hydrogen stream (H2) as raw materials. Equation of the production process is shown as follows [3]:

$$\text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3$$  \hspace{0.5cm} (1)

At present, the energy consumed by industrial ammonia production accounts for more than 1% of the world power supply every year [4]. Therefore, it is necessary to overcome the limitations of Haber-Bosch process, e.g., high energy consumption, high carbon emission, and complex plant equipment, and develop green and sustainable ammonia production process under ambient temperature and pressure with appropriate catalysts [5]. Inspired by nature, researchers have found that many plants can convert nitrogen from air into nitrogen fertilizer and provide nutrients for their growth through nitrogenase produced by microorganisms in their
roots. This process happens at ambient temperature and pressure, and the reaction equation is as follows:

\[ \text{N}_2 + 8\text{H}^+ + 8e^- + 16\text{ATP} \rightarrow 2\text{NH}_3 + \text{H}_2 + 16\text{ADP} + 16\text{Pi} \]  
(2)

It can be seen from this equation that the biological nitrogen fixation process is mainly to provide protons and electrons to nitrogen. Under the catalysis of the nitrogenase, which is dominated by MoFe protein, nitrogen reduction can be achieved to produce ammonia at room temperature and pressure. Based on this strategy, researchers attempt to use electrochemical methods to provide electrons for the nitrogen-fixing reaction, and select the appropriate electrolyte solution to provide the proton source for converting the nitrogen to ammonia. In view of the above analysis, in recent years, many research teams turn to electrocatalytic nitrogen fixation and ammonia production in reaction devices containing nitrogen and water. The reaction formula is shown as follows:

\[ 2\text{N}_2 + 6\text{H}_2\text{O} \rightarrow 4\text{NH}_3 + 3\text{O}_2 \]  
(3)

Under ambient temperature and pressure, electrocatalytic nitrogen fixation for ammonia production possesses the following advantages: (1) nitrogen and water are abundant and easily available on earth; (2) compared with the traditional Haber-Bosch process, it can save equipment and operation costs to a large extent; (3) milder reaction conditions and lower energy consumption. What is more, because the energy in the electrochemical ammonia production process can be converted from solar energy, wind energy, and other sustainable energy sources, it has attracted the attention due to the reasonable and low-cost reaction paths [6]. Though great effort has been devoted to studying on electrochemical nitrogen fixation, how to design suitable catalysts to improve catalytic selectivity and efficiency is the main challenge in this direction [7]. Therefore, the design of catalyst becomes the core component of electrocatalytic ammonia production [8].

Generally, there are three types of the main catalytic materials in the field of electrocatalysis: noble metal catalysts, nonnoble metal catalysts, and metal-free catalysts [9]. It is reported that platinum- and gold-based precious metals show excellent electrocatalytic efficiencies in various redox reactions. However, due to the expensive properties of such electrocatalysts, it is difficult to meet the industry’s demands. Therefore, nonmetallic catalysts have the advantages of low pollution and cheap, which have attracted the attention of researchers while poor conductivity and low electrocatalytic performance still hamper the practical utilization in various applications, such as CO₂ reduction, water splitting, and fine chemical production.

Recently, two-dimensional (2D) materials have attracted great interest in environmental catalysis due to their unique layered structures, which offer us to make use of their electronic and structural characteristics [10]. MXenes are novel two-dimensional nanomaterials, consisting of transition metal nitride and carbide, which are extensively reported [11–13]. This review paper systematically introduces the crystal and electronic structures of MXenes, efficient synthesis methods, and their applications in electrocatalytic reduction of nitrogen. Finally, we still summarize the prospects and challenges of MXene material in photocatalysis, electrocatalysis, and chemical synthesis, providing insights into the development and application of energy materials.

2. Short Summaries of MXenes

Ultrathin two-dimensional nanomaterial MXenes belong to a new class of nanomaterial, which is the general term of transition metal nitride, carbides, or carbonitride compounds. Its structural formulas can be divided into two categories: \( M_{n+1}X_n \) and \( M_{n+1}X_nT_x \), where \( M, X, \) and \( T \) refers to transition metals (e.g., Sc, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, and so on), N or C elements, and the terminal functional group (such as OH, O, or F groups), respectively. And subscript \( n \) is usually an integer from 1 to 3 [14]. MXenes are usually produced through selective etching the most active A element from its corresponding three-dimensional (3D) layered ternary carbide or nitride (MAX phase). The general formula of MAX material is \( M_{n+1}AX_n \) (\( n = 1, 2, 3 \)), in which A stands for IIIA or IVA element, e.g., Al and Si [15]. The relationship between MAX phase and MXenes phase is shown in Figure 1(a) [14]. For example, the MXene material Ti₃C₂ was obtained by etching Al from the Ti₃AlC₂ precursor due to the weak interaction forces between the atomic layer A and the atomic layer MX. Furthermore, the functional groups generated during the etching process endow MXenes good hydrophilicity, but affect its conductivity significantly. For example, single-layer Ti₃C₂ with -O terminal possesses the electron migration rate in \( x \) and \( y \) directions of 611 and 254 cm² V⁻¹ s⁻¹, respectively, and the hole migration rate in \( x \) and \( y \) directions of 74,100 and 22,500 cm² V⁻¹ s⁻¹, respectively [16].

2.1. Crystal Structures of MXenes. Two-dimensional (2D) materials have attracted wide attention in the past decade because of their ultrathin nanostructures and unique physicochemical properties. Besides, 2D materials have a large specific surface area, which has significant advantages in energy storage and catalytic field. As a typical two-dimensional material, MXene has been studied successively, and its excellent performance has been reported. MXene has a clear lamellar structure after erosion from the bulk precursor, and its lateral size is more than 100 nm, up to several microns or even larger, while the thickness of single nanosheet is just single atom or few atoms thickness (generally less than 5 nm) [16–18]. The MAX phase has a layered structure with nanosheets stacked on top of each other, but the increment in the layer voids of MXene material formed by the etching of MAX phase is conducive to the insertion and extraction of certain ions in the material [19]. In the experimental study, MXenes prepared were layered and stacked together, and their morphologies can be seen through scanning electron microscopy (SEM), as shown in Figure 2 [20].
Figure 1: (a) Relation between MAX phase and its corresponding MXenes. (b) Schematic diagram of the structure of –OH-terminated Ti$_3$C$_2$ after selective etching of Ti$_3$AlC$_2$ (yellow, black, red, and white globoids represent Ti, C, O, and H atoms, respectively).

Figure 2: SEM micrographs for (a) Ti$_3$AlC$_2$ particle before treatment, (b) Ti$_3$AlC$_2$ after HF treatment, (c) Ti$_2$AlC after HF treatment, (d) Ta$_4$AlC$_3$ after HF treatment, (e) TiNbAlC after HF treatment, and (f) Ti$_3$AlCN after HF treatment.
2.2. Mechanical Properties of MXenes. The early study of 2D transition metal carbides (TiC, V2C, Cr2C, Zr2C, Hf2C, Ta2C, Ti3C2, Ta3C2, Ti3C3, and Ta3C4) showed the similar structure to the MAX phases; MXenes might possess metallic properties and high elastic moduli, and their mechanical performance should be obviously better than those of multilayer graphene of similar thickness [21]. Later, Ling's group proved experimentally that Ti3C2T, MXene, incorporated with an electrically neutral polyvinyl alcohol (PVA) to produce Ti3C2T/polymer composite films, has excellent flexibility, good tensile, and high mechanical property, which can be adjusted in a large range [22]. Besides, Guo et al. reported surface functionalization could slow down the collapse of the surface atomic layer of MXene, which will possess excellent mechanical flexibilities with enhanced strengths [23].

2.3. Electrical Structures of MXenes. In terms of electrochemical properties, the intrinsic conductivity of MXenes phase is comparable to that of graphene with similar multilayer structures [24]. Generally, MXene contains carbon layer having the similar properties with graphene. Meanwhile, as it has transition metal layer, it can also display similar properties to transition metal oxide. The former gives it good electrical conductivity, while the latter endows it with good energy storage performance. In addition, because of unique hexagonal lattice symmetry and ultrathin structure, the electron is bound in the ultrathin region displaying excellent metallic conductivity and high and anisotropic carrier mobility [25]. Interestingly, the functional groups have apparent impacts on the electrical properties of MXenes (Figure 1(b)) [26]. It is reported that the pristine MXenes (e.g., Ti3C2) possess metallic features, while MXenes containing the functional groups such as F, O, and OH embody the properties of semiconductors [27]. Some researchers show that the surface functional group can not only provide a platform for heterogeneous catalysts but also act as basic combination sites with other molecules or nanostructures [28].

The special structure of MXenes provides the active sites for reaction, and well mechanical performance can be a reason for stability of the MXenes in aqueous solution. Possessing excellent metallic conductivity, which assures efficient charge-carrier transfer on surfaces and exposed terminal metal sites (for example, Ti, Nb, or V), which might lead to strong redox reactivity, MXenes can be a promising catalyst in electrochemical yield [29].

3. Synthetic Methods of MXenes

In 2011, Naguib et al. synthesized MXene material for the first time, where they used hydrogen fluoride as etchant to etch Ti3AlC2, and then exfoliated it to get Ti3C2. According to the similar routes, Researchers developed more methods to prepare other MXene materials. Up to now, more than 70 kinds of MAX materials have been reported, among which 20 kinds of MXenes have been successfully synthesized so far, including Ti3C2, Ti3C, Ti3CN, Ta3C2, TiNbC, Mo2C, and V3C [20, 30, 31]. Generally speaking, MXenes are always synthesized by two methods, including the etching method. In addition, considering effects of fluoride on materials, the etching methods are further divided into fluorinated method and fluoride-free method, which have been summarized in this review.

3.1. Fluorine-Containing Etching Method

3.1.1. Hydrogen Fluoride (HF) Etching Method. MXene materials are usually prepared by selective etching one layer of the MAX phase, and schematic of the etch and exfoliation steps is presented in Figure 3(a) [20]. Take the preparation process of Ti3C2 as an example: at room temperature, HF with a certain concentration is added to Ti3AlC2, and then the Al atomic layer is etched by HF. After centrifuging to wash by deionized water, a powdered solid is formed. The reaction equation is shown as follows:

\[
\text{Ti}_3\text{AlC}_2(s) + 3\text{HF(aq)} = \text{Ti}_3\text{C}_2(s) + \text{AlF}_3(aq) + \frac{3}{2}\text{H}_2(g) \quad (4)
\]

\[
\text{Ti}_3\text{C}_2(s) + 2\text{HF(aq)} = \text{Ti}_3\text{C}_2\text{F}_2(s) + \text{H}_2(g) \quad (5)
\]

\[
\text{Ti}_3\text{C}_2(s) + 2\text{H}_2\text{O(aq)} = \text{Ti}_3\text{C}_2\text{(OH)}_2(s) + \text{H}_2(g) \quad (6)
\]

In Equations (5) and (6), MXene materials with fluorine ion and the hydroxyl group as terminals are formed, respectively, after further etching reaction, where these two surface terminating ligands are widespread in the etching environment. Thereby, the obtained MXenes often are encapsulated by F- and -OH, resulting in the good dispersion in water. In addition, the resulting MXenes are usually composed of several thin layers superimposed on each other due to incomplete exfoliation and electrostatic aggregation. When ultrasonic operation is used as a post treatment, the thickness of the layered MXenes can reach to 11 ± 3 nm. It has been pointed out in the literature that the smaller particle size of M_{n+1}AX_{n} masterbatch can effectively reduce the required etching time or concentration of HF, so that the synthesized M_{n+1}AX_{n} powders are usually screened by abrasion or ball mill before chemical denuded. Naguib and coworkers successfully prepared V,C by using HF etching V2AlC [32], which has high charge–discharge rates and great potential as electrode material for the battery field.

Other MXenes, such as Ti3C, Ta3C3, Ti3CN, Mo2TiC2, Mo6Ti2C3, Cr3TiC2, (Ti0.5, Nb0.5)C, and (V0.5, Cr0.5)C, also are successfully fabricated by this simple etching method [20, 33]. In most reports, only the MAX phase with Al layer can be easily etched by HF and exfoliated into MXenes [34]. However, 2D Zr3C2Ti2 was successfully produced by Zhou and coworkers through selective etching of AlC3 from an alternative layered ternary precursor Zr3AlC5 beyond MAX phase for the first time, which provides a new avenue for synthesizing Zr- and potentially Hf-containing MXenes [35].

3.1.2. Lithium Fluoride/Hydrogen Chloride (LiF/HCl) Etching Method. Considering the corrosive and harmfulness of HF, other milder and substitutable mixed solutions consisting of lithium fluoride/hydrogen chloride with comparably fast,
safe, novel, and facile route are selected for fulfilling etching reaction, to obtain high-yield MXenes by the single-step method [36, 37]. By adjusting the concentration of HCl in such solution, the etching agent is finely controllable. For example, the synthesis of Ti$_3$C$_2$Tx is put Ti$_3$AlC$_2$ powders into the mixed solutions of LiF and HCl. After a while, the resulting sample is rinsed with deionized water several times to remove by-products. Finally, Ti$_3$C$_2$Tx MXenes are obtained after drying. The reaction equation of the etchant is shown as follows:

$$\text{LiF(aq)} + \text{HCl(aq)} = \text{HF(aq)} + \text{LiCl(aq)} \quad (7)$$

3.1.3. Ammonium Hydrogen Fluoride (NH$_4$HF$_2$) Etching Method. Another gentle method is to use NH$_4$HF$_2$ as an etchant to successfully remove the aluminum layer in Ti$_3$AlC$_2$. This method can also insert ammonia seeds such as NH$_4^+$ or NH$_3$ molecules in the etching reactions [38]. Compared with the HF etching method, MXenes prepared with NH$_4$HF$_2$ as the etchant show more uniformity in the interlayer spacing of the layered structure. This facilitates the insertion of large metal ions, such as sodium (Na$^+$) and potassium (K$^+$), beneficial for electrochemical energy storage and energy conversion applications [27].

3.2. Fluorine-Free Etching Method. As we know, the etchants containing fluoride have some negative effects like HF that is harmful, and meanwhile, MXenes with the F terminal groups have often low electrochemical performance [39]. Therefore, it is meaningful to explore new methods in which the process is totally free of fluorine.

Recently, Li et al. [40] prepared a typical MXenes (Ti$_3$C$_2$T$_x$ (T = -OH, -O)) using an alkali-assisted hydrothermal method instead of the fluorine-containing etching
method (Figure 3(b)). As electrode material without any fluoride terminations in capacitor, the resulting Ti₃C₂Xₓ has higher gravimetric capacitance compared with HF-treated Ti₃C₂Xₓ [41]. This is the first time to obtain extremely high-purity multilayer MXenes (92 wt%) merely through NaOH-etching, which opens a new way to synthesize MXenes safely and environmentally.

3.3. Chemical Vapor Deposition Method (CVD). The preparation methods of MXenes mentioned above are selective etching A atoms (A = Al, Si, etc.) from precursor MAX phases and the surface groups (F, O, OH). However, the bottom-up synthesis methods, such as chemical vapor deposition, can also apply to synthesis MXenes [41]. Wang et al. [42] heated copper/molybdenum thin substrate to 1096 °C under hydrogen atmosphere and kept it at a high temperature. Subsequently, CH₄ gas was added to synthesize ultrathin two-dimensional a-Mo₂C crystal successfully. The a-Mo₂C crystal prepared by chemical vapor deposition has excellent chemical, a large lateral size, few defects, and thermal stability. Using the same method, other transition metal carbides, which contain tungsten and tantalum, were made into ultrathin WC and TaC crystals [43]. Currently, this method to synthesize MXene monolayers still should be further explored.

4. DFT Calculation

Density functional theory (DFT) calculation can provide an approximate description of the chemical bond of reaction process in a large variety of systems. Until now, it is not clear to know the paths of the reduction of N₂ on different catalysts, and five paths shown in Figure 4(a) are generally accepted [44]. As a typical reduction reaction, the fixation of nitrogen can be analyzed by this method to predict the reaction pathway and obtain potential high-efficient catalysts.

MXenes have good electrocatalytic activity for nitrogen adsorption and reduction. And this catalytic activity relies on the types of transition metal contained in the material, such as d2: Ti, Zr, Hf; d3: V, Nb, Ta; and d4: Cr and Mo. In other words, only parts of the MXenes prepared have electrocatalytic properties for nitrogen reduction reaction. Azofra et al. [44] performed DFT theoretical calculation on the nitrogen reduction process of d²-d⁴ metallic carbides (MXenes) and concluded that V₂C₂ and Nb₂C₂ are the most promising materials with low activation energy barriers. During the electrocatalytic process over MXenes, the weakening and subsequent activations of the triple bond in N₂ molecule are spontaneous.

Shao and coworkers presented N₂ conversion to ammonia over MXenes with MₓX structures (M = Mo, W, Ta, or Ti; X = C or N) based on the first-principle study [11]. They report that two-dimensional (2D) WₓC and MoₓC monolayers for N₂ fixation have higher efficiencies compared with other considered MXenes because most of the steps are exothermic reactions in general and there is a relatively low reaction energy over 2D WₓC and MoₓC as electrocatalysts.

Furthermore, Luo et al. carried out theoretical calculation of DFT to investigate the active site of N₂ adsorption by MXenes [45]. It is concluded that in the Ti₃C₂O₂ structure (Figure 4(b)), Ti atom is the most active site for the N₂ capture process, which has the largest adsorption energy to N₂ molecule. It is found that Ti₃C₂O₂ presents a single-layered and sandwich structure, in which NRR has two different sites, namely, the terminal O atoms on the base plane and the exposed Ti atom exposed on the edge plane. Through theoretical calculation, the base planes of MXene with oxygen terminal have to overcome the higher energy barrier to realize NRR process compared with the Ti atom, so that N₂ fixation preferred to implement the edge planes with exposed Ti position.

DFT calculation is also carried out to acquire an approximation of the Gibbs free energy of different reactions. Skulason et al. demonstrated that the hydrogen evolution reaction occurs in the reduction of N₂ and is a main competitive process to NRR on most of transition metal electrocatalysts through an early DFT study [46]. The decreased selectivity of catalysts for NRR process is primarily caused by the dominant HER at negative potentials, since the reduction of protons for HER on the surface of catalysts requires less overpotential compared with NRR. Therefore, it is urgent to make efforts to inhibit hydrogen evolution and increase the selectivity for N₂ reduction.

Although the theoretical calculations may underestimate the input energy needed for the reduction process of N₂ to NH₃, this method forcefully demonstrates that the tendency of ammonia reduction on MXene materials is proper and valuable. Therefore, the DFT calculation can be used to calculate the properties of materials, which can combine with the values from experiments for providing deep insight into the fundamental basis of experimental research.

5. Electrocatalytic Reduction of Nitrogen by MXenes

Electrochemical energy storage and energy conversion plays an important role in solving energy shortage and providing clean renewable energy strategies. Considering the excellent structure and electrical properties of MXene materials, MXene and its composite materials have shown practical value in many energy storages fields, such as air batteries and hydrogen storage [47–49]. As newly developed 2D materials with excellent electrochemical activity, stability, and ease of functionalization, MXenes exhibit attractive chemical performance in electrocatalysis and photocatalysis. However, there are few reports on the summary of MXenes in these fields yet. No matter theoretical or experimental studies, only a few catalytic reactions have been recently reported with MXenes in recent years, including CO oxidation [50, 51], oxygen reduction reaction (ORR) [52], oxygen evolution reaction (OER) [53], and hydrogen evolution reaction (HER) [54]. Electrocatalytic reduction of nitrogen to produce ammonia is a frontier research. The development of MXene material as electrode catalytic material is also gradually increasing. The research on the electrocatalytic reduction of nitrogen performance of MXenes is mainly carried out by density functional theory (DFT) calculation and experimental research.
Recent studies have shown that MXene Ti$_3$C$_2$Tx as an electrocatalyst has a great application prospect in NRR, but there is still a lot of room for improving NH$_3$ yield and Faraday efficiency (FE) [52, 55]. Zhao’s group reported that MXene Ti$_3$C$_2$Tx (T = F, OH) nanosheet [52], as a high-performance 2D electrocatalytic nitrogen fixation catalyst, was used for the conversion of environmental N$_2$ to NH$_3$, with good selectivity. Under the condition of 0.1 M (mol/L) HCl, the ammonia yield of the catalyst can achieve 20.4 μg h$^{-1}$ mg$^{-1}$ cat. Under -0.4 V versus reversible hydrogen electrode (RHE), it has high electrochemical and structural stability with a high Faraday efficiency of 9.3%.

At the same time, Fang et al. used the one-step hydrothermal method to grow TiO$_2$ nanoparticles with rich oxygen vacancies into Ti$_3$C$_2$Tx nanosheets in situ to form (TiO$_2$/Ti$_3$C$_2$Tx) heterostructure materials [56]. Oxygen vacancy is the main active site for NH$_3$ synthesis. The untreated Ti$_3$C$_2$Tx nanocrystals with high conductivity can not only promote the electron transfer but also avoid the self-aggregation of TiO$_2$ nanoparticles. The TiO$_2$/Ti$_3$C$_2$Tx nanohybrid in 0.1 M HCl electrolyte exhibits ammonia yield of 32.17 μg h$^{-1}$ mg$^{-1}$ cat. and Faraday efficiency of 16.17% at -0.55 V and -0.45 V versus RHE, respectively, which is a promising electrocatalyst.

In addition to theoretical calculation, Huang’s group mentioned above also tested the catalytic performance of Ti$_3$C$_2$O$_2$ on nitrogen reduction through experiments [47]. The results showed that the Faraday efficiency of ammonia production at -0.1 V vs. RHE was 4.62%, which was higher than the efficiency of most reactions under ambient conditions [57–59]. In the durability test, ammonia yield and current efficiency did not change significantly, indicating that the material has good stability. Interestingly, as both the precursor and conductive substrate, Ti$_3$C$_2$Tx nanosheet was firstly used for in situ hydrothermal growth of TiO$_2$ nanoparticles by Zhang et al. [60]. The combination of TiO$_2$ particles and Ti$_3$C$_2$Tx nanosheets results in a synergistically catalytic Ti-based nanometer hybrid catalyst that can enhance reduction electrocatalysts of nitrogen, with the NH$_3$ yield of 26.32 μg h$^{-1}$ mg$^{-1}$ cat. at -0.6 vs. RHE. Notably, this nanocomposite also shows good selectivity for NRR and high electrochemical stability.

Various NRR metal electrocatalysts along with similar experimental conditions are summarized and displayed in Figure 4: (a) Proposed routes for the N$_2$ conversion mechanism. (b) Structure of Ti$_3$C$_2$Tx MXene and comparison of the activation barriers on the basal plane and the edge plane.
and a few involve in Ti2CT electrocatalysts, which should be paid attention to by potential in the construction of high-performance, low-cost sheet make it an alternative to graphene, and it has great application and have been widely used in lithium and sodium battery, supercapacitor, photocatalysis, electrocatalysis, etc. In recent years, MXenes have received more and more attention, and have been used as the active site for evolution reaction, in order to improve the ammonia production performance. Therefore, it is necessary to further study the preparation method of MXenes and combine theory with experiments to promote the study on the properties of materials. In addition, according to theoretical calculation, the terminal oxygen on MXenes is often used as the active site for hydrogen evolution reaction and carbon dioxide fixations a competitive reaction of nitrogen reduction, which largely weaken the binding of MXenes to nitrogen and reduce the current. Therefore, the design of MXenes reveals more active sites conducive to nitrogen adsorption, which can improve the selectivity of MXenes and inhibit the hydrogen evolution reaction, in order to improve the ammonia production performance.

MXenes is derived from lamellar MAX phase exfoliation. In recent years, MXenes have received more and more attention and have been widely used in lithium and sodium battery, supercapacitor, photocatalysis, electrocatalysis, etc. The unique properties of two-dimensional MXene sheet make it an alternative to graphene, and it has great potential in the construction of high-performance, low-cost electrocatalysts, which should be paid attention to by researchers in the field of electrocatalysis. It is worth noting that the use of multifunctional 2D MXenes as an effective electrocatalyst for nitrogen reduction may have the following merits: (i) 2D MXenes have significant metal conductivity, which are conducive to efficient carrier gas transfer; (ii) due to the multivalence of metallic element, the terminal metal bits on the surface of two-dimensional MXenes (e.g., Ti, Nb, V, or Ta) have stronger redox activity than the other nonmetallic materials; (iii) two-dimensional MXenes have high stability in water medium; (iv) two-dimensional MXenes with hydrophilic surface can interact strongly with targets or water. For the above reasons, MXenes can be an ideal choice for electrocatalysts.

Opportunities and challenges coexist, and future efforts should be focused on the following aspects to increase the catalytic application of MXenes on NRR. Firstly, in addition to common titanium-based MXenes, more attention should be paid to the synthesis and study of other MXenes containing Mo, V, etc. Besides, the combination of theory calculation and experiments would widen the application areas of MXenes. Moreover, deep understanding of mechanism of the reduction of nitrogen and rigorous designing the materials are desired to promote the selectivity and stability of MXenes. Given continuously devoted efforts, MXenes will be an important material in the field of electrocatalytic nitrogen fixation in the near future.

### 6. Challenges and Perspectives

MXenes have the advantages of high specific surface area, excellent conductivity, well stability, and good hydrophilicity, possessing a broad application prospect in electrocatalysis area. But there are still many problems to be solved. For example, experimental studies mainly focus on Ti3C2Tx and a few involve in Ti2CTx and V2CTx. There is a deep understanding of the structure and performance of these reported MXenes, while the preparation routes and electrocatalytic activities of other MXenes are not enough. On the other hand, quite a few studies on catalytic roles of MXenes in nitrogen reduction have been carried out from view of theoretical calculation. No corresponding materials have been prepared in experimental studies, such as V3C2 and Nb3C2 mentioned above. Therefore, it is necessary to further study the preparation method of MXenes and combine theory with experiment to promote the study on the properties of materials. In addition, according to theoretical calculation, the terminal oxygen on MXenes is often used as the active site for hydrogen evolution reaction and carbon dioxide fixations a competitive reaction of nitrogen reduction, which largely weaken the binding of MXenes to nitrogen and reduce the current. Therefore, the design of MXenes reveals more active sites conducive to nitrogen adsorption, which can improve the selectivity of MXenes and inhibit the hydrogen evolution reaction, in order to improve the ammonia production performance.

Table 1 shows the production rate of MXenes is higher than some metal-based NRR electrocatalysts reported recently, indicating the significance of developing MXenes to the efficient conversion of N2 to NH3.

Table 1: A brief summary of recent experimental studies on NRR using various metal electrocatalysts.

| Cat. | Electrolytes | FE (%) | NH3 production rate (μg h⁻¹ mg⁻¹ cat) | Potential (V vs. RHE) | Refs. |
|------|--------------|--------|-------------------------------------|-----------------------|-------|
| Ti3C2Tx (T = O, OH) | 1 M HCl | 9.1 | 36.9 | -0.3 | [61] |
| Ti3C2Tx (T = F, OH) | 0.1 M HCl | 9.3 | 20.4 | -0.4 | [57] |
| TiO2/Ti3C2Tx | 0.1 M HCl | 16.17 | 32.17 | -0.45 | [57] |
| TiO2/Ti3C2Tx | 0.1 M HCl | 8.4 | 26.32 | -0.6 | [60] |
| MnO2-Ti3C2Tx | 0.1 M HCl | 11.39 | 34.12 | -0.55 | [62] |
| Au/Ti3C2Tx | 0.1 M HCl | 18.34 | 30.06 | -0.2 | [63] |
| Pd0.33C0.67/rGO | 0.1 M KOH | 0.6 | 2.8 | -0.2 | [64] |
| Fe50-N-C | 0.1 M KOH | 56.55 | 7.48 | 0 | [65] |
| Au/CeOx-RGO | 0.1 M HCl | 10.1 | 8.3 | -0.2 | [66] |
| B-TiO2 | 0.1 M Na2SO4 | 3.4 | 14.4 | -0.8 | [67] |
| Au/TiO2 | 0.1 M HCl | 8.11 | 21.4 | -0.2 | [68] |

Conflicts of Interest

There is no conflict of interest regarding the publication of this paper.

Authors’ Contributions

L. Yu and J. Qin contributed equally to this work.

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