

MXene-based catalysts: A review

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ARTICLE INFO

Keywords:

MXenes
Catalysts
Chemical reactions
Hydrogen evolution
Oxygen evolution
Oxygen reduction
Carbon dioxide reduction
CO oxidation

ABSTRACT

Two-dimensional (2D) materials, such as graphene, hexagonal boron nitride, 2D metal–organic frameworks, layered double hydroxides, transition metal dichalcogenides, and MXenes, have garnered significant attention in catalysis due to their exceptional properties and structures. Notably, recent studies have revealed the promising catalytic activity of MXene-based catalysts for many reactions, including hydrogen evolution, oxygen evolution, oxygen reduction, nitrogen reduction, carbon dioxide reduction, alcohol oxidation, hydrogenation, dehydrogenation, methanol conversion, dry reforming of methane, and CO oxidation. This review offers a summary of recent advances in the field, contextualizing the progress made. Additionally, it delves into existing challenges while presenting prospects for future developments in this domain.

1. Introduction

Two-dimensional (2D) materials, including graphene [1,2], hexagonal boron nitride (h-BN) [3], 2D metal–organic frameworks (MOFs) [4], layered double hydroxides (LDHs) [5], transition metal dichalcogenides (TMDs) [6], 2D transition metal carbides [7], and MXenes [8–10] have attracted significant interest owing to their outstanding properties and structures. Consequently, they have shown capabilities in applications in many areas, including catalysis, sensors, nanocomposites, actuators, antimicrobial materials, and electromagnetic interference shielding [11–16]. It is also long known that carbides (noble metals containing carbon) can be alternatives to expensive late transition metals as catalysts to accelerate various reactions [17]. For instance, Levy *et al.* [18] investigated the effect of inserting carbon into tungsten (W), which led to tungsten carbide (WC) formation. Their findings revealed that the catalytic performance of WC was comparable to that of pure metals like platinum in reactions, including the formation of water from hydrogen and oxygen at room temperature, the reduction of tungsten trioxide by hydrogen in the presence of water, and the isomerization of 2,2-dimethylpropane to 2-methylbutane. As for the formation of water from hydrogen and oxygen, the chemisorption of hydrogen and oxygen, and subsequent removal of adsorbed oxygen by hydrogen with the formation of water have been long assessed for platinum (Pt) [19], palladium (Pd) [20], and rhodium (Rh) [21]. However, it is unlikely for these processes to take place on other transition metals because they establish robust interactions with oxygen, hindering its removal. In contrast, primary

outcomes have indicated that the incorporation of carbon into tungsten alters the electron distribution. In other words, carbon significantly decreases the high reactivity of tungsten toward oxygen via the introduction of its valence electrons to those of the metal.

In particular, few-layered transition metal carbides, nitrides, and carbonitrides, called MXenes, are novel groups of 2D nanomaterials that have received great interest worldwide due to their extraordinary chemical and physical characteristics [22–25]. They were discovered in 2011 at Drexel University, and since then, research on these 2D materials has exponentially increased [26]. MXenes have the general chemical formula of $M_{n+1}X_nT_x$ ($n = 1–4$), where M is an early transition metal (including Sc, Ti, Zr, Hf, V, Nb, Ta, Cr, and Mo), X is a carbon and/or nitrogen atom, and T_x denotes surface terminations (hydroxyl, oxygen, fluorine, etc.) [27,28]. So far, more than 50 types of MXenes have been synthesized. $Ti_3C_2T_x$ is the most widely studied MXene.

MXenes have been synthesized using different methods. A widely-used method is the selective etching of A element from a ternary $M_{n+1}AX_n$ phase called a MAX phase, where A is an element of the IIIA or IVA group. Single- or a-few-layer MXenes are obtained by the exfoliation and delamination of multi-layer MXenes (Fig. 1) [29–31]. It should be noted that the interlayer bonds are much weaker than intralayer ones in the MAX phase, so a robust etchant can detach the A layer from the MAX structure [32]. Etching by hydrofluoric acid (HF) was the first experimental way of obtaining MXenes [33]. However, HF is corrosive and poses a severe threat to the environment, which has necessitated the development of alternative synthesis methods and the optimization of

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<https://doi.org/10.1016/j.mtcata.2024.100054>

Received 31 January 2024; Received in revised form 7 May 2024; Accepted 8 May 2024

Available online 27 May 2024

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the synthesis steps [9]. Alternative synthesis methods include Lewis acidic etching [34,35], molten salt etching [36,37], electrochemical etching [38], and alkali etching [39]. As a “non-etching” method, chemical vapor deposition (CVD) is a direct synthesis route of MXenes, which results in new morphologies with more easily accessible surfaces and exposed catalytically active edges. In this method, MXenes are fabricated at high temperatures by reacting gaseous precursors, such as a mixture of CH_4 and TiCl_4 , on a substrate [40]. Fig. 2 presents some of the fluoride-containing and fluoride-free synthesis routes of MXenes. As Fig. 2(a) shows, Al atoms in the MAX phase are etched out by HF, leading to the production of a MXene [26]. Another approach involves etching Ti_3AlC_2 initially with a solution of hydrochloric acid (HCl) and lithium fluoride (LiF). Subsequently, the product, $\text{Ti}_3\text{C}_2\text{T}_x$, was repeatedly washed with water to increase the pH to 4–6. Finally, the products were sonicated under inert gas flow, leading to the fabrication of a delaminated $\text{Ti}_3\text{C}_2\text{T}_x$ suspension. To avoid using direct HF directly, a milder LiF initially reacted with HCl to produce HF in this method (Fig. 2 (b)) [41]. Halim *et al.* [42] produced epitaxial MXene films. First, the Ti_3AlC_2 nanometer film was deposited onto a sapphire (0001) substrate via magnetron sputtering (note that a TiC layer was initially formed as an incubation layer). Afterward, the Al layer was removed by an aqueous HF etchant, resulting in $\text{Ti}_3\text{C}_2\text{T}_x$ MXene (Fig. 2(c)). Yang and coworkers [43] conducted a study on the fabrication of exfoliated $\text{Ti}_3\text{C}_2\text{T}_x$ utilizing an efficient fluoride-free etching method based on the anodic corrosion of Ti_3AlC_2 in a binary aqueous electrolyte comprising NH_4Cl and tetramethylammonium hydroxide (TMA-OH). In this process, aluminum was dissolved, followed by in-situ intercalation of ammonium hydroxide, which subsequently led to the formation of carbide flakes ($\text{Ti}_3\text{C}_2\text{T}_x$, $\text{T} = \text{O}, \text{OH}$) with high yield (over 90%) (Fig. 2(d)).

Due to hazards associated with using hydrochloric acid, fluoride-free methods have been proposed. For instance, Xie *et al.* [44] investigated surface leaching of Ti_3AlC_2 (e-TAC) through a fluoride-free hydrothermal etching method, which leads to the formation of a potential support for Pt nanoparticles (NPs). The novel Pt/e-TAC catalyst exhibited higher chemical stability and oxygen reduction reaction (ORR) activity than a Pt/C catalyst. In another research, Cl-terminated MXenes ($\text{Ti}_3\text{C}_2\text{Cl}_2$) were synthesized using a fluoride-free route. In this procedure, the Ti_3AlC_2 MAX phase initially underwent a replacement reaction with ZnCl_2 , producing a Zn-MAX phase (Ti_3ZnC_2). Next, Cl-terminated MXenes ($\text{Ti}_3\text{C}_2\text{Cl}_2$) were produced using excess ZnCl_2 and exfoliating the Ti_3ZnC_2 (Fig. 2(e)) [45]. UV-induced etching is another pathway to produce MXenes [46]. In this pathway, Ga was selectively removed

(from $\text{Mo}_2\text{Ga}_2\text{C}$), leading to the production of a mesoporous Mo_2CT_x MXene, a potential anode for rechargeable batteries (Fig. 2(f)). MXenes have demonstrated attractive features such as high conductivity, light weight, flexibility, and transparency, making them potential candidates for applications such as electromagnetic interference shielding, flexible optoelectronics, sensors, thermal heaters, and nanocomposites [47].

Etching with HF limits termination groups to $-\text{F}$, $-\text{O}$, and $-\text{OH}$ [48]. Alternatively, etching in molten inorganic salts leads to the fabrication of MXenes with other surface terminations, including $-\text{NH}$, $-\text{S}$, $-\text{Cl}$, $-\text{Se}$, $-\text{Br}$, and $-\text{Te}$ [49]. For instance, the etching of the Ti_3AlC_2 MAX phase in molten ZnCl_2 and other molten Lewis acids at a temperature above 500°C brings about the formation of $\text{Ti}_3\text{C}_2\text{Cl}_2$ MXene containing pure $-\text{Cl}$ termination groups [50]. Likewise, etching with molten Lewis acid CdBr_2 has resulted in preparing Br-terminated $\text{Ti}_3\text{C}_2\text{Br}_2$ and Ti_2CBr_2 MXenes. MXenes synthesized through this strategy have $-\text{Cl}$ and $-\text{Br}$ terminations that form weaker (M–F and M–Br) bonds with transition metals from the outer layers of MXene sheets (Ti, Mo, Nb, V), in comparison to M–F and M–O bonds in MXenes prepared via traditional routes. These surface bonds allow for the occurrence of installation and removal reactions where halide ions, *i.e.*, Cl and Br, exchange for other atoms and functional groups, forming MXenes with tunable terminations. Therefore, these chemical transformations and modifications can enable substantial control over the chemistry, structure, and properties of MXene materials [51].

MXenes with $n > 3$ can be synthesized through epitaxial growth (*e.g.*, depositing alternating layers of nitrogen molecules (N_2) and early transition metal). Computational studies, including density functional theory (DFT) methods have supported the usefulness of this method. In this method, N_2 molecules are initially adsorbed onto the surface of a MXene precursor possessing M_2X stoichiometry, followed by the formation of M_2XN_2 MXenes. In summary, computational studies have shown that the epitaxial growth leads to the synthesis of pristine MXenes with alternating N-transition metal layers, rendering these nanomaterials more layers beyond seven [51].

In recent years, the catalytic activities of MXenes, as heterogeneous catalysts, have been studied for many reactions [52,53]. This has primarily been motivated by the scarcity and high cost of noble metals used in noble-metal-based catalysts [54] and the inexpensiveness and abundance of the elements comprising MXenes [31].

This review paper aims to highlight the most recent advances in applying MXenes as catalysts. This paper describes the latest advances in the use of MXenes as catalysts in electrocatalysis reactions, including

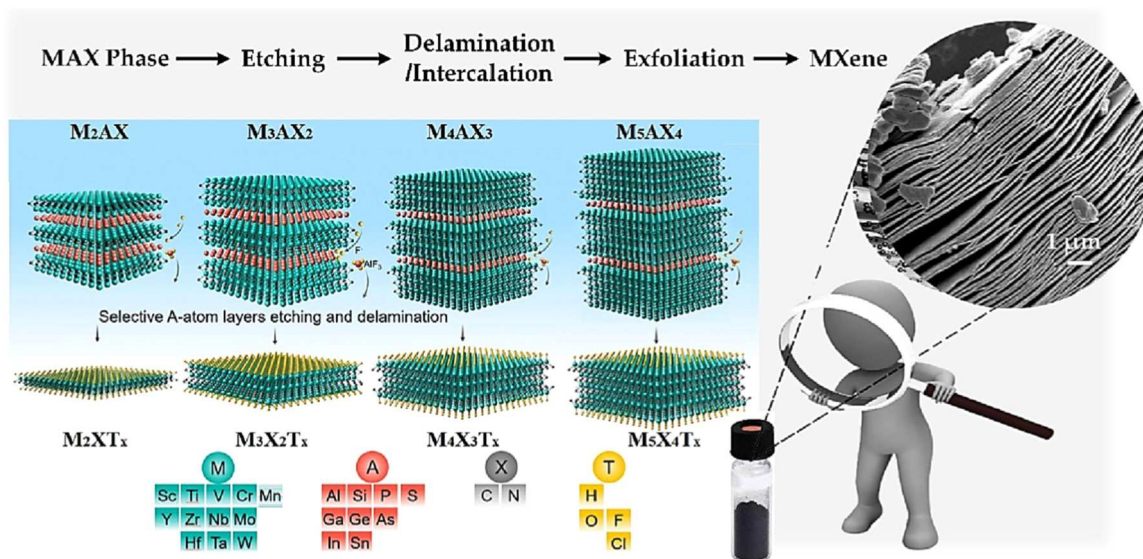


Fig. 1. MXene synthesis involves several steps, including MAX phase preparation, acid etching, and delamination. These steps are shown for a few different MXenes. Reprinted with permission from [9].

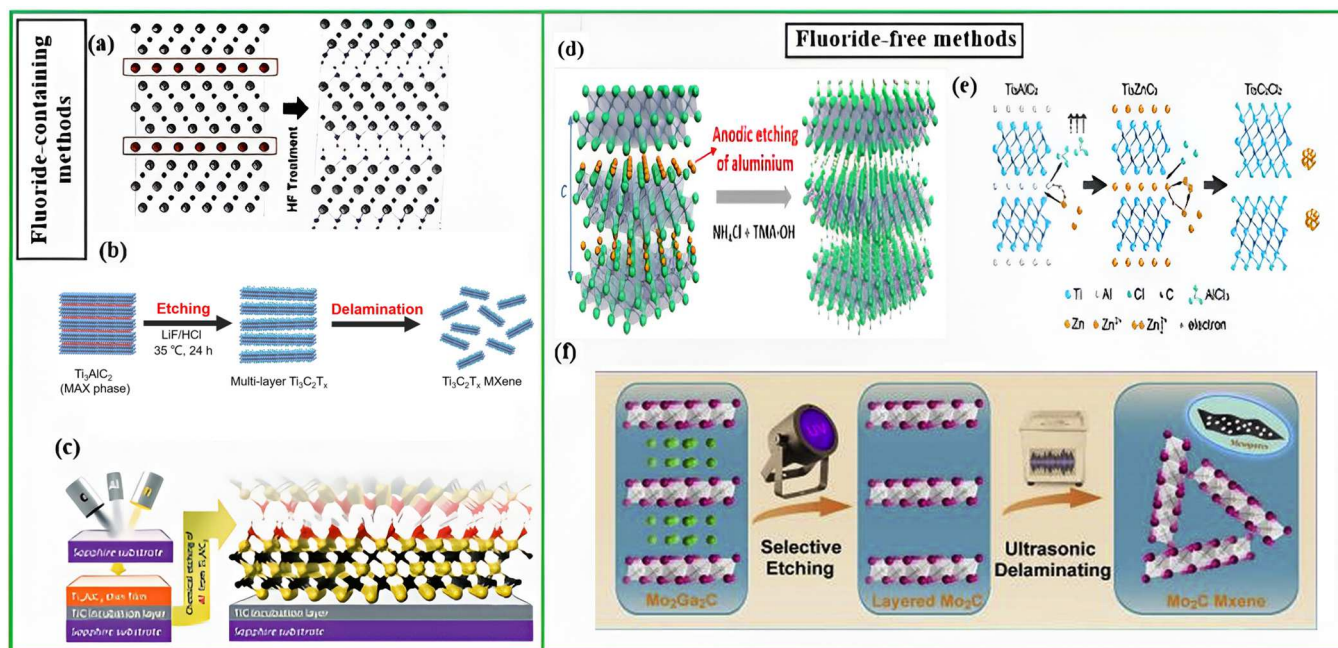


Fig. 2. Schematic illustration of MXene preparation via fluoride-containing and fluoride-free methods: (a) Exfoliation process for Ti_3AlC_2 showing the replacement of Al atoms by $-\text{OH}$ after reaction with HF [26]. (b) MAX phase was etched in a solution of acid and fluoride salt and washed with water to adjust pH toward 4–6. The resulting sediment behaves like clay and can be rolled to produce flexible, freestanding films or molded and dried to yield conducting objects of the desired shape. HCl and milder LiF was used instead of aggressive HF. [41] (c) Schematic diagram of OH-terminated $\text{Ti}_3\text{C}_2\text{T}_x$ after selective etching of Al from the deposited Ti_3AlC_2 by bi-fluoride salts etching [42]. (d) Anodic etching of bulk Ti_3AlC_2 in a binary aqueous electrolyte [43]. (e) The replacement reaction between the MAX phase and late transition-metal halides generates Zn-based MAX phases and Cl-terminated MXenes [45]. (f) UV-induced selective etching route of removing the double Ga layers from $\text{Mo}_2\text{Ga}_2\text{C}$ precursor to generate Mo_2CT_x [46].

(a) Reprinted with permission from [26]. (b) Reprinted with permission from [41]. (c) Reprinted with permission from ref [42]. (d) Reprinted with permission from ref [43]. (e) Reprinted with permission from ref [45]. (f) Reprinted with permission from ref [46].

hydrogen evolution reaction (HER) (Table 1), oxygen evolution reaction (OER), ORR, nitrogen reduction reaction (NRR), carbon dioxide reduction reaction (CO_2RR), and alcohol oxidation reactions (AORs) (Section 2). Photocatalytically-driven reactions, including HER, CO_2RR , NRR, and pollutant degradation reactions, are then considered (Section 3). Next, the use of MXene-based catalysts for other reactions, including hydrogenation and dehydrogenation, methanol (CH_3OH) conversion, dry reforming of methane (DRM), and carbon monoxide (CO) oxidation are covered (Section 4). The article finally ends with a conclusion and perspectives on MXene-based heterogeneous catalysts.

Table 1

Recent reports regarding the application of MXene-based materials for the electrocatalytic hydrogen evolution reaction.

MXene	Electrolyte	Overpotential (mV)	Ref.
$\text{Nb}_4\text{C}_3\text{T}_x$	1.0 M KOH	398	[55]
$\text{Ti}_3\text{C}_2\text{T}_x\text{NF}^a$ s	0.5 M H_2SO_4	169	[56]
$\text{MoS}_2\text{-Ti}_3\text{C}_2\text{T}_x$	0.5 M H_2SO_4	98	[57]
$\text{Mo}_2\text{CT}_x/2\text{H-MoS}_2$	0.5 M H_2SO_4	119	[58]
$\text{MD}^b\text{-Ti}_3\text{C}_2\text{T}_x/\text{MoS}_x$	0.5 M H_2SO_4	196	[59]
$\text{Pd/Nb}_2\text{C-HF}$	0.5 M H_2SO_4	34	[60]
$\text{CoP/Ti}_3\text{C}_2\text{T}_x$	0.5 M H_2SO_4	71	[61]
Ti_2CT_x	0.5 M H_2SO_4	609	[62]
Mo_2CT_x	0.5 M H_2SO_4	283	[62]
$\text{V}_4\text{C}_3\text{T}_x$	0.5 M H_2SO_4	200	[63]
$\text{F-Ti}_2\text{CT}_x$	0.5 M H_2SO_4	170	[64]
$\text{Ti}_3\text{C}_2\text{O}_x$	0.5 M H_2SO_4	190	[65]
$\text{P-Mo}_2\text{CT}_x$	0.5 M H_2SO_4	186	[66]

^a NF = nanofiber

^b MD = modified

2. Electrocatalysis reactions

MXene-based catalysts have been widely studied for electrocatalysis due to their good hydrophilicity, high electrical conductivity owing to lamellar spacing, large surface area, and tunable properties [67–69]. To boost the catalytic activity of MXenes and MXene-based catalysts, strategies including heteroatom doping, structural engineering of defects, interfaces, strain, lateral size, and thickness have been proposed and studied. Also, efforts have been made to tune surface functional groups of MXenes to increase the electrocatalytic reaction rate. For instance, the rates of HER and NRR can be enhanced by increasing the concentrations of O and F functional groups on the surface of MXenes, respectively [70, 71]. MXenes functional groups act as sites for the adsorption of various reactants, thus accelerating electrocatalytic reactions [72,73].

MXenes' electrocatalytic performance can also be boosted by incorporating them with transition metals, metal oxides, metal-free substrates, and other 2D materials because MXenes and these materials display synergic effects, improving the overall electrocatalytic efficiency [67,74,75]. In this section, we aim to describe the general trend and recent developments in electrocatalysis, including water splitting (HER and the OER), ORR, NRR, CO_2RR , and alcohol oxidation reaction (AOR).

2.1. Water splitting

Industrialization and global population growth have compelled societies to utilize massive levels of fossil fuels to meet their energy demands, which in turn have caused severe and alarming issues, most importantly air pollution [76]. Consequently, unprecedented attention has been paid to developing renewable and environmentally friendly energy sources [77]. During the past few years, some alternatives have been proposed, one of which is the water-splitting system, which

decomposes water directly into hydrogen and oxygen [78,79]. Water splitting progresses within two half-reactions: HER at the cathode and OER at the anode. However, the slow rates of HER and OER result in a slow overall water-splitting reaction, which is a roadblock in the production of hydrogen from water via electrocatalysis [80,81]. The widely known water-splitting electrocatalysts are Pt and Ru/Ir-based noble-metal oxides [82–84]. However, these catalysts are scarce in nature, are expensive, and have low stability, which has impeded their applications on large scales. So, finding and producing better electrocatalysts for water-splitting reactions have invariably been a challenge [85–87].

With the discovery of MXenes, the use of MXenes as electrocatalysts or platforms for other catalysts in the water-splitting reaction has been investigated. Due to their exceptional characteristics, MXene-based catalysts have proven efficient in water-splitting reactions. Conducting DFT calculations, Gouveia *et al.* studied water bonding and dissociation on a set of eighteen M_2X MXenes. They concluded that the MXenes can favorably adsorb water in an exothermic reaction, with adsorption energies ranging from 1.43 to -2.94 eV. Additionally, these catalysts can greatly facilitate water splitting with energy barriers below 0.44 eV [88]. As pointed out, water splitting consists of HER and OER, meaning its overall efficiency depends on the respective HER and OER [86]. So, in the following two sub-sections, we will elucidate the HER and OER performance of MXene-based catalysts and summarize recent advances in the use of MXenes as either electrocatalysts or supports.

2.1.1. Hydrogen evolution reaction

Renewable and sustainable energy sources are of primary importance as alternatives to fossil fuels [89]. Hydrogen is an attractive fuel, which can be generated via multifarious reactions known as hydrogen evolution reactions (HERs) [90–97].

In the past few years, several materials, such as noble metals, have been experimented on as catalysts for HER since they can facilitate the low overpotential and increase the rate of H_2 -production reactions owing to the fact that these reactions are usually slow. Nonetheless, these metals lack high efficiency, limiting their applications in HER and other catalytically driven reactions associated with producing renewable substances on industrial scales [98–101]. MXenes have shown catalytic activity in HER, attributed to their exceptional structures and transition metals, which are inexpensive and earth-abundance [102]. The Gibbs free energy of atomic hydrogen adsorption describes the catalytic activity of MXenes in HER. The closer the Gibbs free energy to zero, the higher the activity of MXene catalysts [103]. In this respect, Gao calculated the HER catalytic performance of five oxygen-terminated MXenes, all of which showed a Gibbs free energy of near zero (Fig. 3) [71]. It should be noted that, according to the Sabatier principle, the

binding strength of hydrogen absorption on MXene catalysts should be "just right," meaning it should not be either too strong or too weak [104]. The HER is:



where H^* is active hydrogen adsorbed on the catalyst surface [71]. It is worth mentioning that an acidic medium is better than an alkaline one for HER progression due to the fact that, in contrast to alkaline media, acidic media require lower overpotentials to begin the catalysis, which is imperative for HER initiation [105].

HER kinetics was found to involve two intermediate steps with three possible pathways, the Volmer, and the Heyrovsky or Tafel (Fig. 4). The first step of HER is called the Volmer reaction, in which a water molecule is adsorbed onto the catalyst surface (in an alkaline media). The second step depends on the concentration of active sites on the catalyst surface, meaning surfaces with low and high concentrations of active sites follow the Heyrovsky or Tafel pathway, respectively. Likewise, the same would happen in an acidic solution [106].

Employing Pourbaix diagrams, Meng and coworkers [107] investigated the effect of mixed surface terminations on the HER performance of MXenes. They considered nearly 450 topologically various surface terminations, encompassing $Ti_3C_2T_x$ with no terminations, full $-O$, $-OH$, $-F$, and $-H$ terminations, and their different compositions. Based on realistic models derived from Pourbaix diagrams, they concluded that models close to HER equilibrium line, namely $O_{2/3}OH_{1/3}$, $F_{1/3}O_{1/3}OH_{1/3}$, and $F_{3/9}O_{4/9}OH_{2/9}$, demand a negligible overpotential of 0.01 V, showing their potential for use on the surfaces of MXenes for electrocatalytic HER.

Although the HER catalytic performance of MXene-based substances is typically satisfactory, efforts have been made to further boost their catalytic activity in HER. Some progress has been made in this regard, among which controlling surface functional groups [71,108,109], tailoring the structures [110–112], doping with other materials [113–115], and hybridization [102] have proved to be effective (Fig. 5). Recent research on MXenes and their nanocomposites for utilization in HER are summarized in Table 1.

2.1.2. Oxygen evolution reaction

Oxygen evolution reaction (OER) is a reaction by which oxygen molecules are generated through water electrolysis [117]. OER is conducted via two commonly plausible mechanisms, i.e., adsorbate evolution reaction (AER) and lattice-oxygen mediated reaction (LOM) (Fig. 6) [118–121]. In the former, an alkaline medium is preferable over an acidic one since OER suffers from sluggish kinetics in acidic media [86].

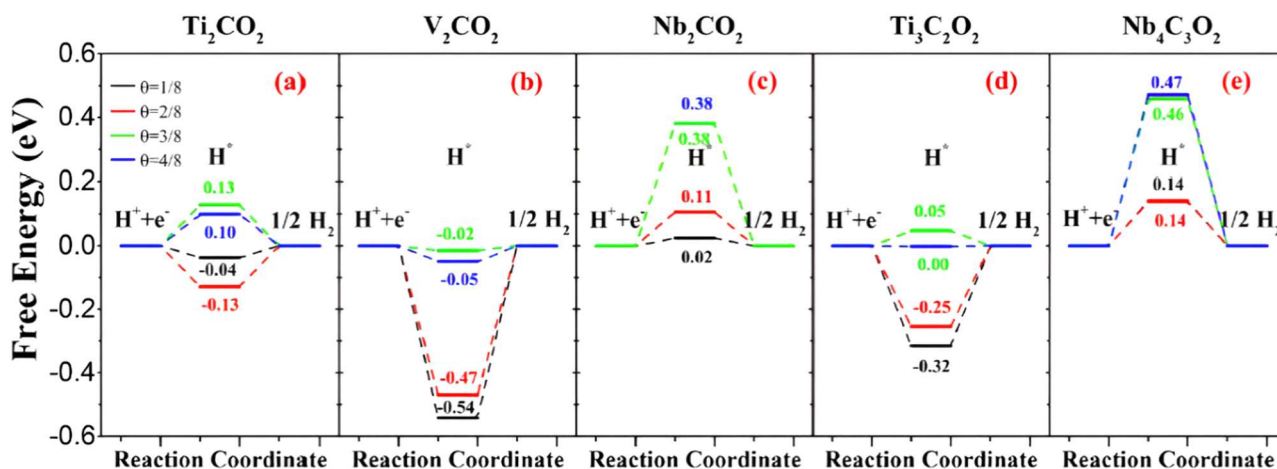


Fig. 3. Free energy diagram of HER on five MXenes (Ti_2CO_2 , V_2CO_2 , Nb_2CO_2 , $Ti_3C_2O_2$, and $Nb_4C_3O_2$) under standard conditions [pH = 0, $p(H_2) = 1$ bar, $U = 0$ V] vs. a standard hydrogen electrode. θ denotes the hydrogen coverage in H^* adsorption. Reprinted with permission from [71].

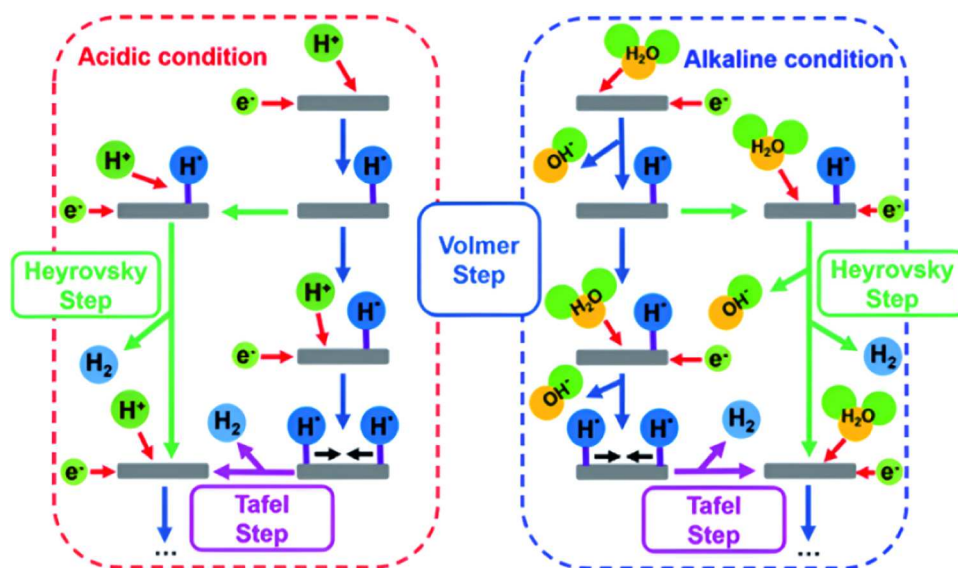


Fig. 4. HER mechanism in acidic and alkaline conditions with the Volmer (blue), Heyrovsky (green), and Tafel (purple) reaction steps. There are two well-defined pathways for HER: Volmer-Heyrovsky and Volmer-Tafel. In an alkaline condition, the reaction begins with the adsorption of a water molecule (Volmer step). If the catalyst surface contains low concentrations of active sites, the Heyrovsky step occurs where another water molecule is adsorbed, followed by OH^- and H_2 desorption. Otherwise, the Tafel step takes place where the desorption of H_2 is provoked by two active sites close to each other. The distance between the two active sites should not exceed the van der Waals radius of two adsorbed hydrogen atoms. Reprinted with permission from [106].

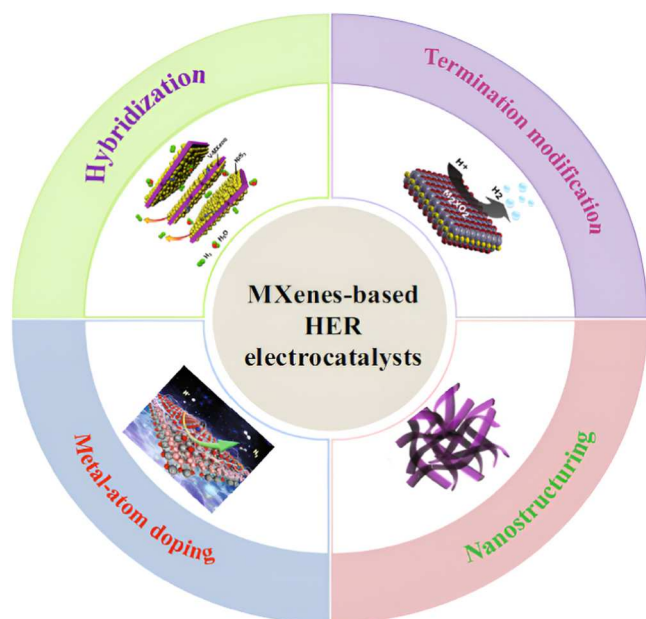


Fig. 5. Approaches for optimizing HER electrocatalytic performance of MXene-based materials. The optimization of MXene surface terminations positively affects the electronic structure and electron transfer (top right). The hybridization of MXenes with other active materials has been demonstrated to synergistically promote HER activity, such as chalcogenides, layered hydroxides, phosphides, metal nanoparticles/alloys, carbides, and even metal-free black phosphorus (top left). The doping of metal atoms can establish new active sites for the adsorption of hydrogen molecules to further drive HER (down left). Nanostructuring is another solution for improving MXenes' HER activity by accelerating the electrochemical response, creating more special electronic properties, and providing abundant active sites (down right). Reprinted with permission from [116].

It should be noted that although LOM is a potential pathway for OER, only a few investigations have assessed this mechanism so far [122,123].

Similar to HER, OER suffers from sluggish kinetics, so

electrocatalysts, such as Ru, Ir-based catalysts, metal oxides, metal sulfides, and metal phosphides, are imperative to boost the reaction rate [122,124–127]. However, the activities or stabilities of these catalysts usually deteriorate due to OER's harsh operating conditions and catalyst particles agglomerate, compelling the incorporation of support materials to immobilize catalyst particles [128]. Doing so prevents particle agglomeration and improves catalyst activity and stability, leading to the production of more efficient electrocatalysts for OER [129–132]. Due to their unique properties, MXenes seem to be paramount electrocatalyst supports for OER. For instance, Liu *et al.* [133] synthesized MXene-supported NiMn-LDHs through a simple hydrothermal pathway (Fig. 7). Aberration-corrected scanning transmission electron microscopy (Ac-STEM) confirmed the construction of 2D NiMn-LDHs and 2D $\text{Ti}_3\text{C}_2\text{T}_x$. The results demonstrated that although poor electrical conductivity of LDHs hampers their applications in OERs, their deposition on MXenes can substantially improve their overall performance in electrolysis. The reason for boosting the electrocatalytic performance is the coupling effect between the utilized MXene ($\text{Ti}_3\text{C}_2\text{T}_x$) and NiMn-LDHs, which effectively narrowed the bandgap of NiMn-LDHs and regulated their electronic structures, thus ameliorating the OER efficiency and reaction kinetics.

MXenes as catalyst supports should have several important properties. For example, they should prevent the catalysts from being agglomerated, ensuring high specific surface areas (SSAs) of the catalysts [134]. For example, Zhao *et al.* [75] synthesized a 2D porous $\text{Ti}_3\text{C}_2\text{T}_x$ -supported cobalt 1,4-benzene dicarboxylate (CoBDC) catalyst as an effective OER catalyst. The outcomes showed that $\text{Ti}_3\text{C}_2\text{T}_x$ could greatly enhance SSA (from 106.6 to 199.1 m^2g^{-1}) by preventing CoBDC particles from being agglomerated, exposing more nanocatalysts. In another research, Han and coworkers [135] investigated the effect of CoS_2 introduction between $\text{Ti}_3\text{C}_2\text{T}_x$ sheets. They concluded that not only can the MXene hinder the agglomeration of CoS_2 particles, but also CoS_2 prevents the restacking of the MXene nanosheets, improving the overall SSA (from 6.4 to 46.2 m^2g^{-1}). Hao *et al.* [136] fabricated a vertical array structure of CoFe-LDH on $\text{Ti}_3\text{C}_2\text{T}_x$ support and discovered that the MXene could significantly enhance SSA.

Another pivotal characteristic that MXene supports should contain is the ability to improve electrical conductivity. It is evident that MXenes with the most efficient and optimal conductivity are promising options

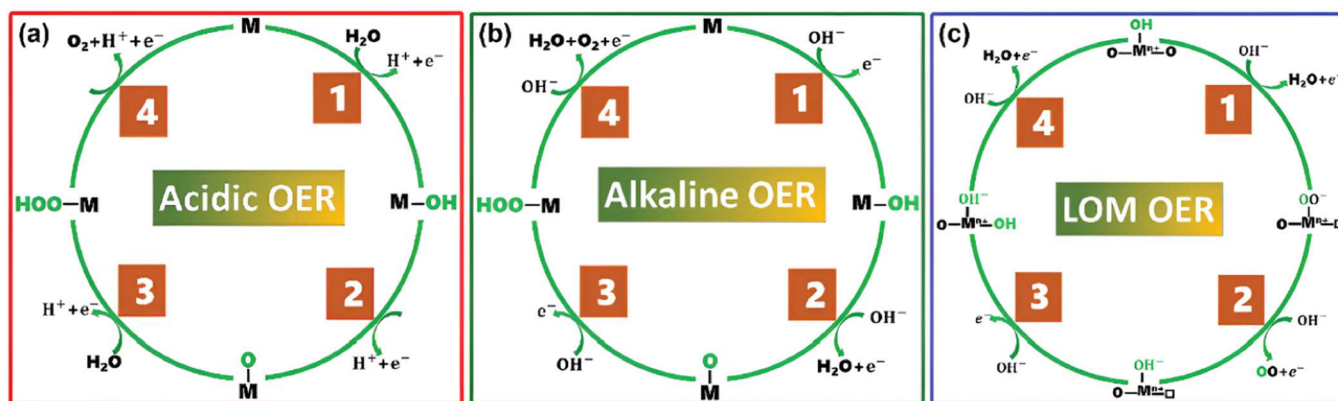


Fig. 6. Adsorbate evolution mechanism (AEM) of OER in an (a) acidic and (b) alkaline medium. (c) Lattice-oxygen mediated mechanism (LOM) of OER. M and □ denote an active site and an oxygen vacancy, respectively. The release of the lattice oxygen ligand from the catalyst is accompanied by the formation of oxygen vacancy, which is replenished and then acts as a new active center. Reprinted with permission from [117].

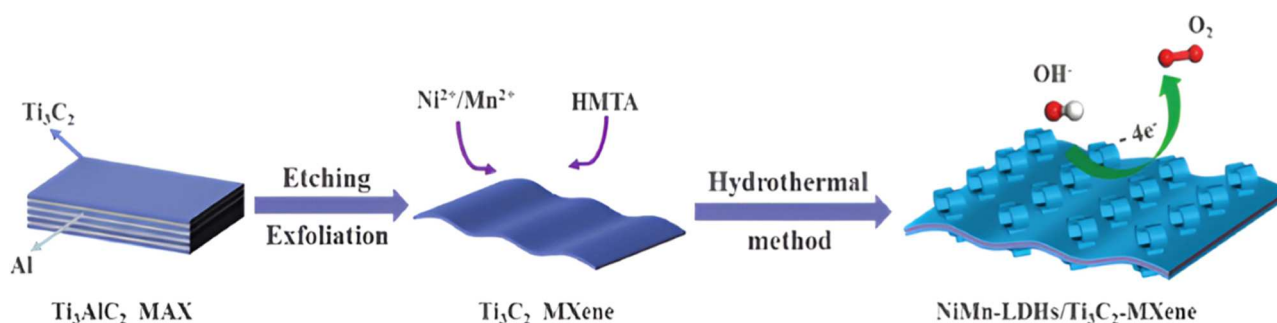


Fig. 7. An illustration of the hydrothermal method for NiMn-LDHs/Ti₃C₂T_x-MXene hybrids preparation. Reprinted with permission from [133].

as supports for OER catalysts owing to the fact that they can facilitate charge transfer across the catalysts [117]. For example, Yu and co-workers [137] reported that the addition of Ti₃C₂T_x to FeNi-LDH reduced the charge transfer resistances (R_{ct}) of FeNi-LDH from 24.7 to 5.1 Ω . OER overpotentials associated with/without the harness of MXenes as supports for layered triple hydroxides (LTH) and LDH are summarized in Table 2. Metal-support solid interaction (SMSI) also plays a crucial role in boosting electron transfer from the catalyst to the MXene. The surface functionality of MXenes changes the electronic structure of catalysts, establishing strong interfacial interactions between catalysts and MXenes. As MXenes can attract electrons quickly, they can quickly transfer them to the supported catalyst [138].

Another attractive property of MXene-supported catalysts is their hydrophilic behavior, which benefits OER. This property is rooted in MXenes' abundant functional groups (F/O/OH/Cl), which can interact with water molecules. Recent research has concluded that MXene-catalyst compounds possess substantial hydrophilicity [117]. To illustrate, Si *et al.* [145] measured the contact angle (CA) of the

NiFe-LDH/Ti₃C₂T_x/nickel foam (NF) compound. The outcomes showed that NiFe-LDH/Ti₃C₂T_x/NF had a contact angle $\approx 0^\circ$ (Fig. 8a), demonstrating its hydrophilic behavior. On the contrary, the CA of NF and NiFe-LDH/NF were 119.7° (Fig. 8b) and 86.2° (Fig. 8c), respectively. Intense interactions between MXene and water molecules can result in more oxygen adsorption, eventually augmenting OER activity [146]. Furthermore, MXene supports can make electrolysis catalysts more chemically stable and corrosive resistant than those not deposited on MXenes [147]. It should be noted that C-containing MXenes are more chemically stable than those containing N atoms [147].

2.2. Oxygen reduction reaction

Oxygen reduction reaction (ORR) is one of the most vital processes in clean energy industries, specifically in fuel cells. ORR is feasible through two main, *i.e.*, the following four-electron and two-electron pathways [148], both of which can be progressed and accelerated by various kinds of catalysts [149]:



It is worth mentioning that a direct reaction between H₂ and O₂ can produce hydrogen peroxide (H₂O₂). Nevertheless, this reaction route has a high risk of explosion and lacks an appropriate level of selectivity owing to the dilution to reduce safety ventures [150,151].

Carbon-supported electrocatalysts utilized in ORR usually suffer from carrier corrosion, leading to the instability of catalysts [152–154]. In the past few years, several studies have been conducted on the corrosion resistance of MXenes as promising candidates in ORR. Having anti-corrosive properties, MXenes have been proven to prevent their

Table 2

OER performance of LDH/LTH electrocatalysts with/without Ti₃C₂T_x support.

Catalyst	OER overpotential [mV] at 10 mA cm ⁻²		Reference
	-Without Ti ₃ C ₂ T _x	With Ti ₃ C ₂ T _x	
NiFe-LDH	-	235	[139]
Co ₄ MnFe ₃ -LTH	370	263	[140]
NiFeCe-LDH	302	260	[141]
RuCo-LDH	-	330	[142]
Co-LDH	390	340	[128]
NiMn-LDH	356	294	[133]
Cr-Fe-Ni-LDH	280	232	[143]
NiCo-LDH	600	300	[144]

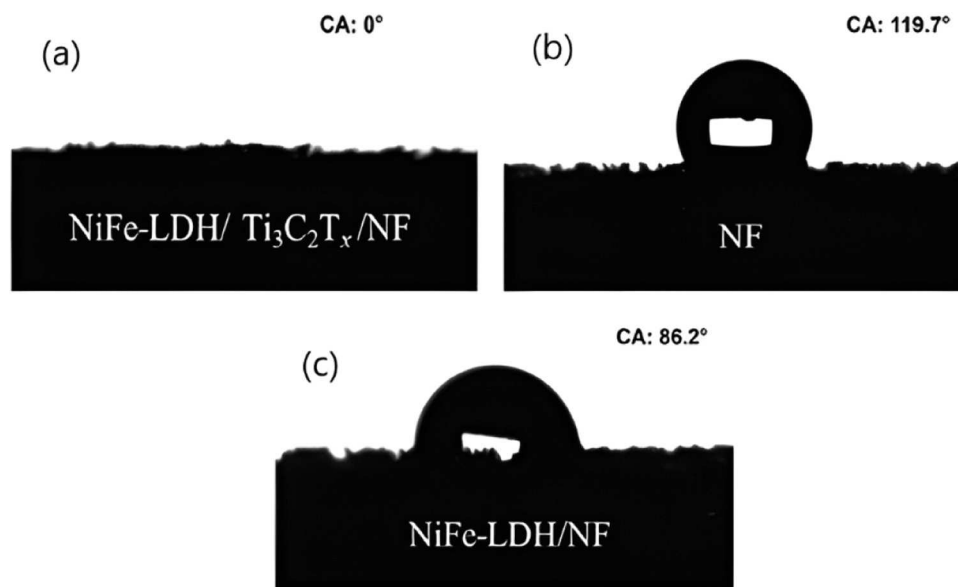


Fig. 8. The contact angle of (a) NiFe-LDH/Ti₃C₂T_x/NF, (b) NF, and (c) NiFe-LDH/NF electrodes. Reprinted with permission from [145].

supported catalysts from being unstable [155]. Moreover, MXenes can diminish the potential barrier for driving electrons across the catalysts and improve charge transfer, thereby making the catalytic activity more efficient [131]. Lastly, despite possessing favorable activity, Pt-based catalysts are not cost-effective and accessible, calling for less costly and more abundant catalysts like MXenes [156,157]. There have been several articles reviewing recent trends and developments in the field of MXene-based materials for ORR. For example, Lin and coworkers [158] assessed the ORR catalytic performance of 2D single-layered (SL) Ti₃C₂T_x nanosheets. They found that the ORR onset potential associated with SL Ti₃C₂T_x was much more than the reversible hydrogen electrode (RHE). Moreover, the charge transfer resistance of SL Ti₃C₂T_x on the electrode surface measured via electrochemical impedance spectroscopy (EIS) was found to be higher than those of multilayered (ML) Ti₃C₂T_x and Ti₃AlC₂, supporting the improved ORR catalytic activity of SL Ti₃C₂T_x. Furthermore, in the possession of their large surface area, 2D MXenes can adsorb many oxygen molecules to accelerate ORR.

Pt-based electrocatalysts are among the most paramount candidates in ORR. However, Pt is expensive and has low accessibility and relatively low stability. As a result, fabricating inexpensive, earth-abundant, and stable catalysts is desirable in clean energy industries [159]. Metal-nitrogen/carbon nanocomposites (M-N/C, which M stands for Fe, Co, Ni, and Cu) are among the most promising alternatives to Pt-based

catalysts for ORR due to their beneficial characteristics, including high nature-abundance, high efficiency, and low cost [160,161]. Despite these merits, the performance of M-N/C substances is unsatisfactory, necessitating the development of novel materials that meet the requirements for ORR [162].

In recent years, MXene supports for M-C/N in ORR have been investigated [163,164]. A case in point is a report by Chen *et al.* [165], who developed Ti₃C₂T_x-supported-non-precious-metal iron-cobalt (Fe-Co) nanoparticles. This study unraveled the role of Ti₃O₂ as a hindrance to Co-Fe nanoparticles' agglomeration, resulting in higher catalytic performance owing to the higher exposed surface area. In another study, Zhang *et al.* [166] investigated the ORR and OER catalytic efficacy of nitrogen-doped multi-walled carbon nanotubes incorporated with Co (Co/N-CNTs) with a Ti₃C₂T_x support. The linear sweep voltammogram (LSV) curve (Fig. 9 a) suggests that (Co/N-CNTs)@Ti₃C₂T_x can outperform the catalyst lacking Ti₃C₂T_x due to its improved electron transfer characteristics. As the LSV curve demonstrates, the (Co/N-CNTs)@Ti₃C₂T_x composite possesses significantly enhanced ORR activity due to the synergetic effect between Co/N-CNTs and Ti₃C₂T_x MXene. Chen *et al.* [167] prepared cobalt-tipped carbon nanotubes integrated with Ti₃C₂T_x (Co-CNT/Ti₃C₂T_x), in which zeolitic imidazolate framework-67 (ZIF-67) nanoparticles were in-situ grown and exposed to a pyrolysis reaction. Their findings indicate that Co-CNT/Ti₃C₂T_x was

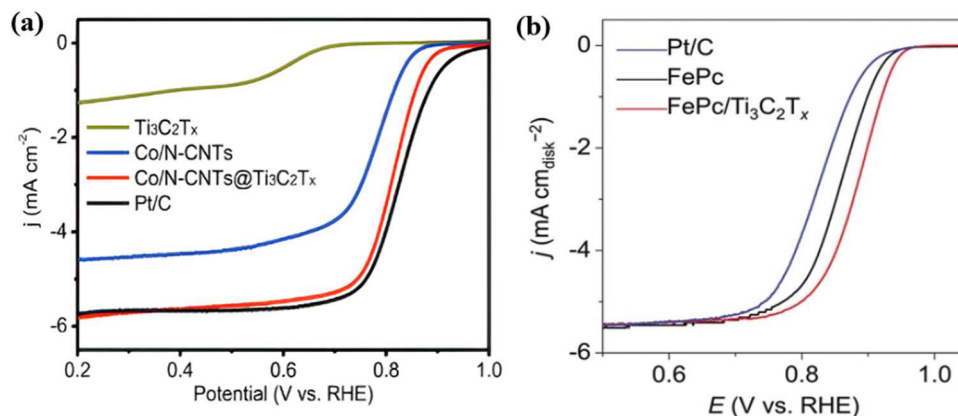


Fig. 9. LSV curves of (a) pristine Ti₃C₂T_x, CO/N-CNTs, CO/N-CNTs@Ti₃C₂T_x, and the Pt/C benchmark, and (b) Pt/C, FePc, and FePc/Ti₃C₂T_x. (a) Reprinted with permission from [166]. (b) reprinted with permission from [168].

highly active as an electrocatalyst for ORR. This enhancement was attributed to Co-CNT/Ti₃C₂T_x high surface area, abundant Co-C/N site on the tips of CNTs, and virtually high graphitization of carbon. While Co-CNT/Ti₃C₂T_x represented relatively analogous ORR activity, it had superior stability than Pt/C-based catalysts. In another study, Li *et al.* [168] investigated the ORR activity of a pristine iron phthalocyanine (FePc) catalyst (an early Fe–N–C prototype with typical FeN₄ moiety and very Pt-like ORR activity) following the introduction of Ti₃C₂T_x as a support. This coupling caused remarkable Fe 3d electron delocalization and spin configuration changes, which made the active FeC₄ sites more readily adsorb reaction species involved, therefore improving the ORR performance. Their LSV results (Fig. 9b) suggested a positive shift of ≈ 26 mV compared to that of 0.86 V vs. RHE for pure FePc.

Several research studies have reported the utilization of MXene-assisted catalysts to accelerate OER and ORR. However, only a few studies have mentioned the potential instability of MXenes in oxidative environments of OER and ORR. For instance, Kuznetsov *et al.* [169] experimentally studied the substitution of Mo sites on Mo₂CT_x MXene by Fe single atoms (Mo₂CT_x:Fe) to verify increased stability and activity following the incorporation of Fe atoms. Characterization results unraveled the in-situ evolution of Mo₂CT_x:Fe to Fe oxyhydroxide (ferrihydrite, Fh) species distributed on a graphitic carbon framework (Fh/C), acting as the main active parts. As a result of the difference between the stability of Mo and Fe, Mo was selectively etched out of Mo₂CT_x, which led to the fabrication of graphitic carbon onto which Fh clusters were distributed, affirming poor stability of pure Mo₂CT_x in the oxidative situations of OER and ORR in basic conditions. Computational calculations have also been conducted to scrutinize the stability of MXenes under electrocatalytic reaction conditions [170]. Tsounis *et al.* [171] plotted the Pourbaix diagrams of Mo₂CO₂ and V₂CO₂ to assess the (in)stability window of these MXenes in electrochemical reactions, namely OER and ORR. They reported that these pristine MXenes (and possibly other counterparts) are stable at “negative” potentials and high pH. Therefore, Pourbaix diagrams highlight the effect of anodic potentials on the stability of MXenes. Furthermore, the largest window in which the oxidative decomposition of MXenes takes place is in solutions with high pH. As a result, caution must be taken when using MXenes at high pH and high anodic potentials, since the oxidative decomposition is still likely. Therefore, pristine MXenes are potentially appropriate as sole catalysts when used in reactions that occur at potentials near that of HER or lower (e.g., those of N₂, CO₂ and NO₃ reduction); i.e., near or below 0 V vs. RHE, and at a low pH.

2.3. Nitrogen reduction reaction

N₂, as one of the most paramount components of the atmosphere, serves as a pivotal molecule for a sustainable and environmentally friendly pathway of producing ammonia (NH₃) [172]. From a common industrial point of view, NH₃ can be produced through a conventional reaction called the Harber-Bosch (HB) process, in which N₂ and H₂ are the correspondent feedstock, with metals being the reaction catalysts. Nonetheless, this process necessitates tremendous energy (a temperature above 350 °C and a pressure above 150 atm). Furthermore, the raw materials employed in the HB process are derived from petroleum, leading to their accumulation in the atmosphere and contributing to the generation of CO₂ [173]. Consequently, a renewable pathway of NH₃ generation has always been a preoccupation for researchers in the past few decades. In the natural process of NH₃ synthesis, N₂ and water undergo an electrocatalytic reaction under mild conditions, in which H₂ molecules and electrons are derived from H₂O and electricity sources, respectively [174]. However, this route results in low yield and selectivity of NH₃ [175]. In this regard, 2D materials have gained significant attention as alternatives to noble metal catalysts for efficient N₂ fixation and then N₂ conversion to NH₃. This significance is owing to their large surface area and dispersed active sites that they potentially offer for N₂ adsorption and activation [79].

MXenes, as the most promising 2D substances, have proven to be efficient for clean NRR due to their previously mentioned characteristics, for which some review papers have been published in the past few years [176]. From a computational viewpoint, Azofra and coworkers [177] investigated the NRR performance of MXenes. Utilizing DFT, they concluded that MXenes bring about a spontaneous Gibbs free binding energy for N₂ fixation and further activation. Wet-lab research has also been conducted along with computational ones to confirm the NRR efficacy of MXenes. For example, Zhao *et al.* [178] assessed 2D Ti₃C₂T_x (T = F, OH) MXene performance of NRR and attained an NH₃ yield rate of $\approx 20.4 \mu\text{g} \cdot \text{mg}_{\text{cat}}^{-1} \cdot \text{h}^{-1}$. MXene-assisted NRRs proceed through three consecutive steps, namely adsorption and activation, hydrogenation, and desorption. The electrocatalytic-driven mechanisms associated with N₂ reduction to NH₃ fall into two generally accepted pathways of dissociative and associative routes, which differ in their hydrogenation order [179]. The dissociative pathway correlates to the cleavage of the N₂ triple bond in the adsorption stage, which requires an immense level of energy. Subsequently, each separated N atom goes through independent hydrogenation reactions, followed by desorption from the catalyst surface (Fig. 10a). The requisite harsh condition (high temperature and pressure) in the HB process is due to this mechanism (for breaking the N₂ triple bond). On the other hand, the associative takes place so that the N₂ triple bond is not dissociated during adsorption but happens at a particular stage in hydrogenation. This pathway is divided into three distinctive sub-pathways called alternating, distal, and enzymatic (Fig. 10b) [180].

While there is no general rule for predicting the precise pathway by which NRR progresses, research studies have demonstrated that different MXenes follow different NRR mechanisms. For instance, Xia *et al.* [181] studied the NRR electrocatalytic performance of V₂CT_x. Via DFT calculations, they discovered that this MXene could result in the NH₃ rate of $12.6 \mu\text{g h}^{-1} \text{mg}_{\text{cat}}^{-1}$ and Faradaic efficiency (FE) of 4% at -0.7 V in the M Na₂SO₄ media through a distal mechanism. Lastly, it is noteworthy that various parameters, including morphology [182], surface terminations [183], and incorporation of other materials [184–187], affect the electrocatalytic efficacy of MXenes. MXenes-doped with nanomaterials have also enhanced NRR electrocatalytic activity compared to pristine MXenes. In a case DFT study, Zheng and coworkers [188] incorporated Boron (B) sites as doping agents onto Mo₂CO₂ and W₂CO₂ MXene surfaces, resulting in a remarkably increased catalytic performance and improved selectivity in NRR. The modeled B-doped Mo₂CO₂ and W₂CO₂ MXenes showed limiting potentials of -0.20 and -0.24 V, respectively. Previous research results associated with the electrocatalytic NRR application of MXenes and MXene-based materials are summarized in Table 3.

2.4. Carbon dioxide reduction reaction

The greenhouse effect caused by industrialization has resulted in the accumulation of contaminant gases, on top of which is CO₂. Therefore, researchers have been endeavoring to diminish the CO₂ level by integrating various methods, like recycling, energy recovery, biomass utilization, and carbon capture and utilization [194]. During the past few decades, some research has been conducted on the plausibility of CO₂ conversion into valuable substances through the electrolytic CO₂RR. Nonetheless, the effectiveness of this reaction strongly depends on developing potential and cutting-edge catalysts to ensure the long-run feasibility of CO₂RR on industrial scales [195].

In the possession of exceptional properties mentioned in the previous paragraphs, 2D materials hold promise as potential catalysts for CO₂RR. MXenes are among those 2D electrocatalysts whose CO₂RR efficiency has been investigated within the past few years. Not many studies have been conducted on the CO₂RR performance of MXenes since their potential as heterogeneous catalysts is still in its infancy, so preliminary computational research on this topic was done by Li *et al.* [196]. In this study, they discovered that Cr₃C₂ and Mo₃C₂ MXenes are capable of

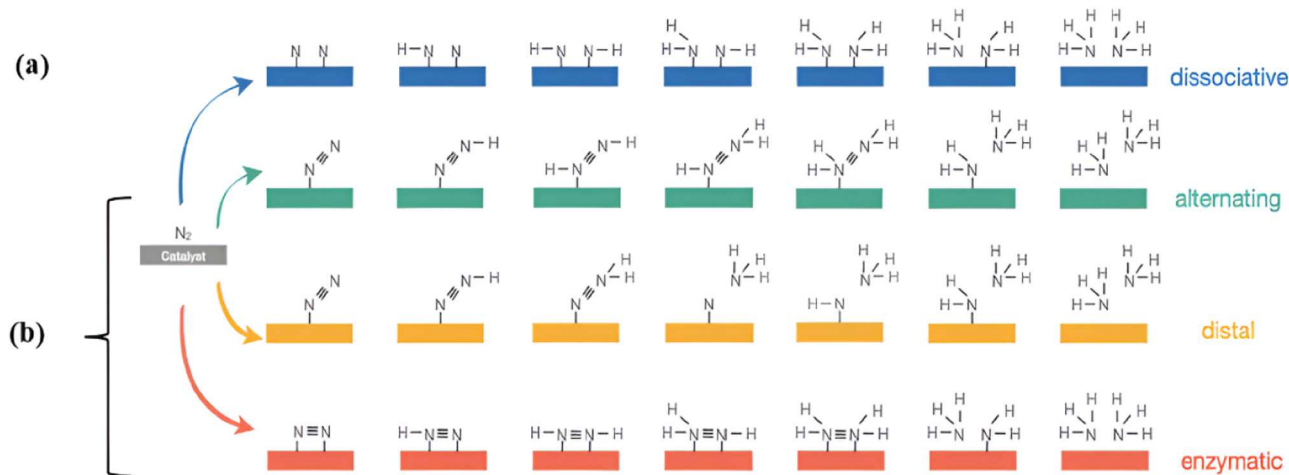


Fig. 10. Schematics of NRR on catalysts via (a) the dissociative and (b) associative pathways. Reprinted with permission from [180].

Table 3

Recent research regarding the electrocatalytic ability of MXenes and MXene-based materials towards NRR.

Catalyst	NH ₃ yield rate	FE (%), potential vs. RHE	N ₂ reduction mechanism	Ref
F-terminated Ti ₃ C ₂ T _x	0.1 μmol•cm ⁻² •h ⁻¹	7.4% at -0.55 V	NR ^a	[189]
Cu/Ti ₃ C ₂ T _x	3.04 μmol•cm ⁻² •h ⁻¹	7.31% at -0.5 V	Distal	[184]
Au/Ti ₃ C ₂ T _x	30.06 μg•mg ⁻¹ •h ⁻¹	18.34% at -0.2 V	Alternating	[190]
Surface-engineered Ti ₃ C ₂ T _x	1.71 μg•cm ⁻² •h ⁻¹	7.01% at -0.2 V	Alternating	[191]
Ti ₃ C ₂ T _x (T= F, OH)	20.4 μg•mg ⁻¹ •h ⁻¹	9.3% at -0.4 V	Distal	[178]
Ru@ Ti ₃ C ₂ T _x	2.3 μmol•cm ⁻² •h ⁻¹	13.13% at -0.4 V	Distal	[192]
V ₂ CT _x	12.6 μg•mg ⁻¹ •h ⁻¹	4% at -0.7 V	Distal	[181]
N-S-doped Ti ₃ C ₂ T _x	34.23 μg•mg ⁻¹ •h ⁻¹	6.6% at -0.55 V	NR ^a	[193]

^a NR = Not reported

converting CO₂ to CH₄, which is a vital energy-generating gas in industries. Other theoretical investigations have also been concentrated on employing MXenes to produce CH₄ [197]. Conversely, in 2020, Handoko *et al.* [198] embarked on an experimental study to explore titanium and molybdenum carbide MXenes for CO₂RR in an effort to expand horizons in the emerging field of MXenes. Unlike preceding computational research in which CH₄ was the predominant CO₂RR product, this study discovered formic acid as the dominant product, with an FE of 56.1% for KF-HCl-etched Ti₂CT_x. It is important to note that the synthesis route of MXenes and CO₂RR experimental conditions can affect the type of reaction products. In another case, Attanayake and coworkers [199] studied the CO₂RR potential of Mo₂CT_x and Ti₃C₂T_x-based MXenes in an acetonitrile-based electrolyte mixture with 1-ethyl-3-methylimidazolium tetrafluoroborate. They found CO to be the primary product of this reaction, with an FE of 90% and 65% for Mo₂CT_x and Ti₃C₂T_x, respectively. Meng *et al.* [200] reviewed the recent advances in DFT calculations on the CO₂RR efficacy of MXenes. They divided models into three generations. The first generation of models (2017–2018) revealed the potential application and high activity of clean MXenes in CO₂ adsorption, even in harsh operational situations, with a maximum CO₂ capture capacity of 8.25 mol.kg⁻¹. These theoretical findings were later validated experimentally, paving the way for

the employment of MXene materials as electrocatalysts in CO₂RR. However, these models suffered from oversimplification and overlooked the effects of surface terminations. The second generation of models (2018–2020) studied the effects of surface terminations, such as -O, -OH, -S, and -F, on CO₂ and other intermediates binding energies. Different intermediates may react with surface groups via the H, C, or O atoms. Nevertheless, interaction with H atoms of the -OH-containing terminations may either simplify proton-couples electron transfers or lead to the stability of intermediates by as-generated surface -O group after -H removal from -OH. The third generation of models (2020–present) revealed the significant role of vacancies in modifying intermediate binding energies. They also showed that the vacancies have more paramount influences on the reduction of H⁺ than the binding of CO₂ during the process.

Various techniques have been exploited to tune the activity and selectivity of MXene-based catalysts in CO₂RR, such as controlling surface vacancies [201], doping [202], and incorporating multiple components into MXenes [203]. Concerning metal-doped MXenes, Eid *et al.* [201] investigated the CO₂RR performance of Cu/Ti₃C₂T_x MXene. They found that the Cu/Ti₃C₂T_x catalyst outperformed pristine Ti₃C₂T_x, with a formic acid FE of 58.1% in Cu/Ti₃C₂T_x and ~18.7% in Ti₃C₂T_x, respectively (Fig. 11a). In another DFT study, Cheng *et al.* [204] assessed the CO₂RR efficiency of pristine Nb₂CO₂ and nonmetallic and metallic-doped Nb₂CO₂ (N- and Cu-doped Nb₂CO₂). Their results indicated that N- and Cu-doped specimens possessed lower reaction Gibbs free energy than pure Nb₂CO₂ (Fig. 11(b-d)), demonstrating higher activity towards CO₂RR. Kannan *et al.* [205] also investigated the effect of iron-doped-zinc oxide (ZnO-Fe) on the Ti₃C₂T_x-based electrochemical reduction (eCR) of CO₂. They found the current density of ZnO, Ti₃C₂T_x, ZnO-Fe, ZnO-Ti₃C₂T_x, and ZnO-Fe-Ti₃C₂T_x to be 3.439, 6.64, 7.13, 10.21, and 18.745 mA/cm², respectively, under an applied potential of 0.2 V, thus indicating the high activity of ZnO-Fe-Ti₃C₂T_x towards CO₂RR.

2.5. Methanol and ethanol oxidization reactions

Direct alcohol fuel cells (DAFCs) have attracted interest in generating electricity from commonly known alcohols, *i.e.*, CH₃OH and ethanol (C₂H₆O), as they have advantages such as convenient energy transformation, low noise, and high efficiency [14]. In the past few years, Pt-based catalysts supported by carbon have been widely used as potential electrocatalysts in DAFC processes [206,207]. Nonetheless, there are several bottlenecks with Pt, including its high cost, alcohol crossover, long-run instability, and CO poisoning [208]. Furthermore, some carbon supports used to immobilize Pt-based catalysts usually suffer from corrosion-induced degradation and low graphitization. Therefore,

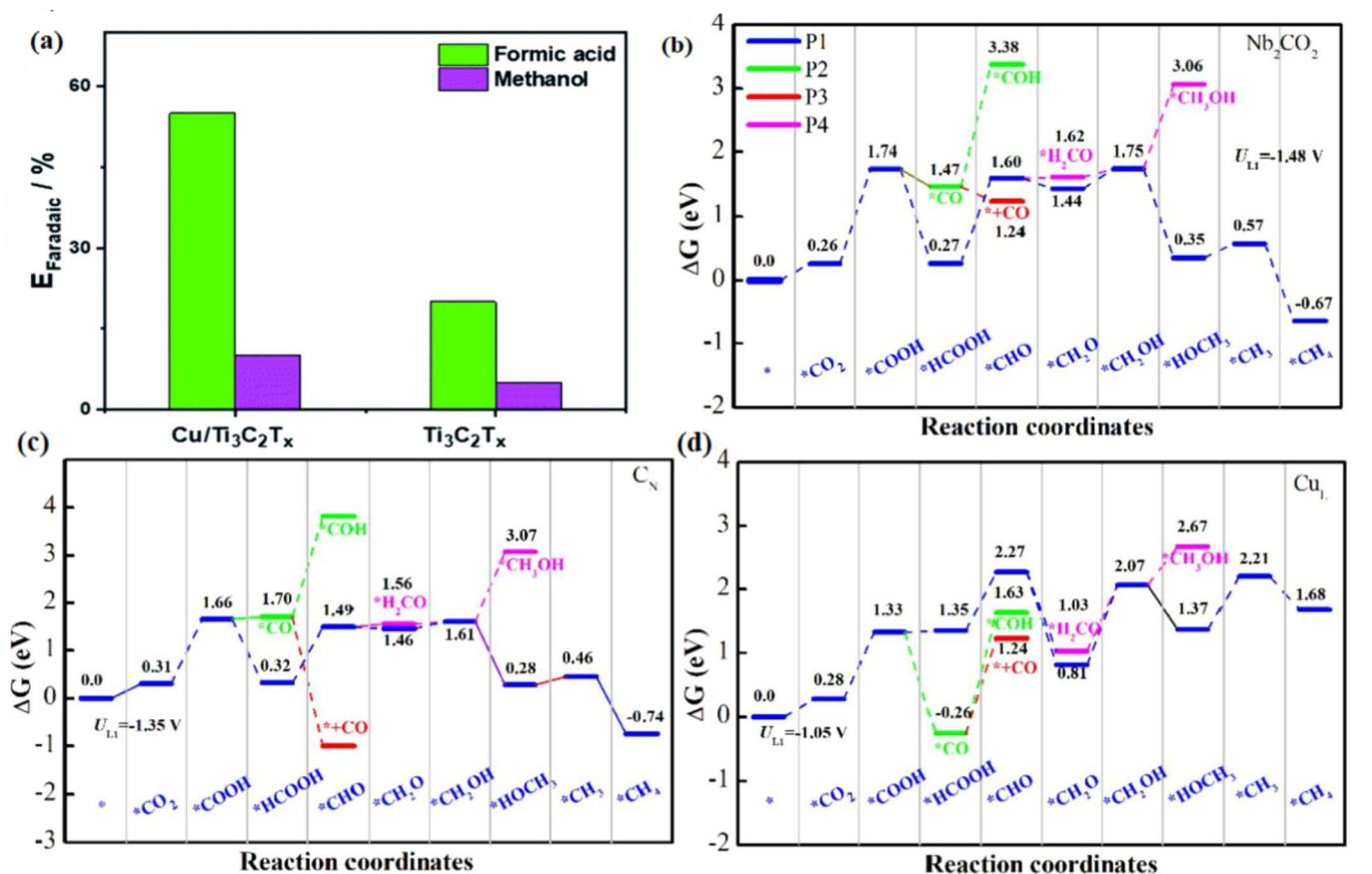


Fig. 11. (a) Comparison of the FE products between pristine Ti₃C₂T_x and Cu-doped-Ti₃C₂T_x. (b) Reaction Gibbs free energy plots of CO₂RR on (b) pure Nb₂CO₂, (c) N-doped-Nb₂CO₂, and (d) Cu-doped-Nb₂CO₂ surfaces. Note that P1, P2, P3, and P4 illustrate different pathways of CO₂RR on Nb₂CO₂-based catalysts, corresponding to different Gibbs free energies.

(a) Reprinted with permission from [201]. (b) B-d: Reprinted with permission from [204].

efforts have been made to harness carbon supports with superior characteristics beneficial to DAFC or develop strategies to mitigate their corrosion. For example, Zhao *et al.* [209] investigated different methods to reduce carbon corrosion. However, they discovered that carbon corrosion and degradation remain significant challenges despite these corrosion diminishment strategies. Considering these challenges, researchers have fabricated low-carbon or free-carbon supports, such as metal dioxides (TiO₂, IrO₂, WO₃, and SnO₂) [210], nitrates, and carbides (SiC, TiC, and B₄C) [211]. Apart from these materials, MXenes have also gained particular interest because of their well-defined characteristics. DFT calculations showed that MXene supports, specifically Ti-based ones, can establish favorable adsorption energy for depositing necessary noble metals and other catalysts [212,213]. Experimental investigations revealed that Ti-based MXenes are highly efficient for MOR and that Ti₃C₂T_x MXene enriched Ti–O terminals exhibit a high electrical conductivity and a large specific area, leading to improved electrochemical performance in MOR. The prepared specimen demonstrated an onset potential of -0.51 V, with long-term stability and durability toward MOR [214].

To date, several review articles have represented the potential of harnessing metal and non-metal-supported MXenes. However, as mentioned in the previously elucidated paragraphs, the utilization of MXenes in catalytic reactions is still at the nascent stage [79,215–218]. As a result, in this paper, we review some of the most novel updates on MXenes MOR and EOR performance, whose valuable outcomes have been represented in Table 4. As pointed out, Pt is among the widely used electrocatalysts for MOR and EOR purposes. However, due to the issues mentioned at the beginning of this section, they should be immobilized into 2D substances to ensure their stability and durability. MXenes have

been shown to hold promises as support for Pt and many other catalysts. A few studies have focused on MXenes-supported Pt, the first of which conducted by Wang *et al.* [219] reported a peak current density for Pt/Ti₃C₂T_x three times higher than a conventional carbon-supported Pt (Fig. 12a and b), indicating that Pt/Ti₃C₂T_x is a promising candidate for MOR. Furthermore, transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) analyses illustrated that Pt nanoparticles were successfully deposited and distributed on the Ti₃C₂T_x surface, guaranteeing a high surface area for adsorption and activation (Fig. 12c and d). In terms of stability of the Ti₃C₂T_x support, the calculated electrochemical surface area (ECSA) Pt/Ti₃C₂T_x was 30.2 m²/g, and it lost only 15% of its surface electrochemical stability toward Pt immobilization. In contrast, the correspondent loss was 47% for Pt/C.

2.6. Nitrate reduction reaction

With the rapid discharge of industrial wastewater, a vast amount of nitrate (NO₃) enters water grounds, calling for urgent actions to remove them to provide global populations with drinking water and prevent individuals from getting fatal diseases such as liver cancer and gastric cancer [230–233]. Currently, two leading technologies exist for the removal of NO₃ from water: reverse osmosis and biological denitrification. However, the former suffers from high expenses and the latter from creating byproducts caused by the metabolism of microorganisms, leading to secondary pollution to the water body [234,235].

Electrocatalytic nitrate reduction has garnered substantial interest in converting NO₃ into harmless substances, including N₂ and NH₃, as industrial raw materials, which demands low energy consumption and

Table 4

Recent studies on the electrochemical performance of MXene support for MOR/EOR.

Catalyst	ECSA (m ² /g)	Specific activity (mA cm ⁻²)	Methanol oxidation peak current (mA cm ⁻²)	Stability (Retention rate)	Ref
Ni(3%wt) MoS ₂ /Ti ₃ C ₂ T _x	1.17 ^a	NR ^b	7.7	78.4%/ 500 cycles	[220]
Pt/Ti ₃ C ₂ T _x	30.2	NR ^b	1.137	85%/ 1000 cycles	[219]
Pd/Ti ₃ C ₂ T _x -rGO (1:1)	97.97	25.47	NR ^b	NR ^a	[221]
Pt/(RGO) ₃ -Ti ₃ C ₂ T _x	90.1	NR ^b	NR ^b	24.4%/ 1000 cycles	[222]
Pd/Ti ₃ C ₂ T _x @NG ^c	34.5	6.56	NR ^b	31.4%/ 500 cycles	[223]
NiCu-LDH/Ti ₃ C ₂ T _x (45%wt)	7.625 ^a	11.39	86.9	77.8%/ 500 cycles	[224]
Pt NW ^d /PDDA ^e -Ti ₃ C ₂ T _x	61	NR ^b	17.2	NR ^b	[225]
Pt ₆₉ Rh ₈ Fe ₂₃ -PNS ^f @Ti ₃ C ₂ T _x	46.4	NR ^b	NR ^b	72.8%/ 1000 cycles	[226]
Pt-on-Pd/Ti ₃ C ₂ T _x	157.3	0.93	NR ^b	62.9%/ 200 cycles	[227]
PtRu/Ti ₃ C ₂ T _x	54.91	NR ^b	22.9	NR ^a	[228]
Pd/GO ₅ -Ti ₃ C ₂ T _x -PS	89.9	NR ^b	NR ^b	55.4%/ 800 cycles	[229]

^a = unit: cm²^b NR = Not reported^c NG = nitrogen-doped graphene^d NW = worm-shaped nanocrystals^e PDDA = poly(diallyldimethyl-ammonium chloride)^f PNS = porous ternary nanosphere.

diminished environmental pollution [236]. Nonetheless, owing to the lack of high selectivity for nitrate reduction reaction (NITRR) to NH₃, harnessing electrocatalysts is vital to ensure the long-term feasibility of this reaction on industrial scales [237]. Moreover, one of the challenges in NITRR is the competence with HER and the production of byproducts like H₂, which decreases the efficiency of this reaction [238].

Given the extraordinary characteristics mentioned in the previous sections, 2D MXenes have attracted attention in NITRR [239]. For instance, Hu *et al.* [240] assessed the potential use of MXenes as electrocatalysts in NITRR (converting NO₃ to NH₃) via DFT calculations. They concluded that MXenes could drive NITRR through their basal planes, where NO₃ was readily deoxygenated, while the subsequent hydrogenation was challenging. Combining MXenes and NITRR bimetallic catalysts, such as Fe-Mo [241], Cu-Rh [242], and Cu-Fe [243], can improve charge transfer and exposure of active sites, thus increasing overall catalytic performance. In another research, Zhang *et al.* [244] incorporated highly dispersed Bi₂O₃ electrocatalyst on Ti₃C₂T_x nanosheets, in which oxygen vacancies facilitated electron transfer and exposed more active sites. Meanwhile, Bi₂O₃ inhibited HER, further boosting the overall NITRR efficiency (NH₃ yield rate of ~ 7.0 mg•cm⁻²•h⁻¹). Nevertheless, these catalysts might lose their stability on the surface of MXenes due to the insufficiency of MXene surface functional groups (-F, -OH, etc.), which necessitates the application of negatively charged surface functional groups of MXenes to establish robust interactions with cationic metals, or the solid interfacial polarization of MXenes to catalyze the breaking of N-O bonds [245–247]. Additionally, MXenes themselves suffer from issues such as collapsing, causing decreased electron transfers and catalytic performance. This shortcoming can be partially addressed through adjusting the interfacial states, functional groups, and defect states, utilizing confinement effects to load single atoms, constructing heterogeneous structures, and

creating interfacial polarization [245].

3. Photocatalysis reactions

Photo-induced reactions (harnessing sunlight) hold promise as alternative routes to developing and producing clean energies [248]. More specifically, photocatalytic reactions are crucial in water splitting, CO₂RR, NRR, and pollutant degradation. MXenes are promising candidates for this purpose owing to their superior properties over other catalysts [54,249–251]. This section describes different MXenes photocatalytic applications in the pertinent reactions, including water splitting, CO₂RR, NRR, and pollutant degradation.

3.1. Water splitting

There are various technologies for hydrogen and oxygen clean production, among which the water splitting innovation offers more benefits such as inexpensiveness, convenience, and being environmentally friendly [252]. A photo-driven water splitting reaction follows these three preliminary steps: 1) light absorption by the semiconductor photocatalyst and generation of photogenerated charge carriers, meaning electrons (e⁻) and holes (h⁺), 2) migration of electrons and holes from the bulk to the surface of the photocatalyst, and 3) the contribution of electrons and holes to the redox reactions directed into H₂ and O₂ generation [253]. Unlike computational research investigating the “excited states,” namely excitons of traditional photocatalysts like rutile TiO₂ (110), the assessment of MXenes for their photocatalytic activity is often based on their band gap size and alignment [254–256]. This section describes recent investigations and advances in the area of H₂ generation using MXene photocatalytic HER.

3.1.1. Hydrogen evolution reaction

Hydrogen is the primary molecule for the production of ammonia and a vital substance in petrochemical industries. However, there are some challenges with its production by conventional methods like exploiting fossil fuels. The water-splitting reaction has shown promise in H₂ generation to meet global demands. This reaction occurs in the presence of a semiconductor photocatalyst and sunlight illumination, proceeding a reaction independent of hazardous fossil fuels. The reaction mechanism is the same as described previously, *i.e.*, Volmer–Tafel or Volmer–Heyrovsky pathways [257]. Nonetheless, photocatalytic water splitting lacks high efficiency on industrial scales. Therefore, efforts have been made to enhance the reaction performance using cocatalysts [253,258]. Cocatalysts extract charge carriers from the correspondent photocatalyst surface and hinder their recombination, improving HER rate and yield [259].

MXenes have attracted prominent attraction as HER cocatalysts owing to their high electrical conductivity, which is beneficial to electron transport to the surface of the photocatalysts [71]. DFT calculations have proven MXenes’ co-catalytic performance. For instance, Ran and coworkers [260] investigated the co-catalytic activity of Ti₃C₂O₂ MXene deposited on a CdS photo-absorber. They discovered that the ΔG_{H⁺} of this MXene was close to zero at ½ H* coverage (Fig. 13a), thus boosting the HER performance compared to traditional catalysts, namely Pt, MoS₂, and WS₂ (Fig. 13b).

MXenes can also be employed as direct HER photocatalysts with suitable valence band (VB) and conduction band (CB) potentials [85]. To illustrate, Ti₃C₂T_x MXene is applicable as an HER photocatalyst since it offers advantages like a hydrophilic surface and a Gibbs-free adsorption energy close to zero [261]. Using DFT calculations, Ontiveros *et al.* studied the bandgap of a wide array of MXenes by their structure, composition, and oxygen surface termination to determine appropriate MXenes for photocatalytic water splitting. Their study indicated that C-MXenes possessed more cases with bandgap favorable for water splitting compared to N counterparts. Moreover, the effects of factors such as stacking and specific oxygen-termination hollow sites were

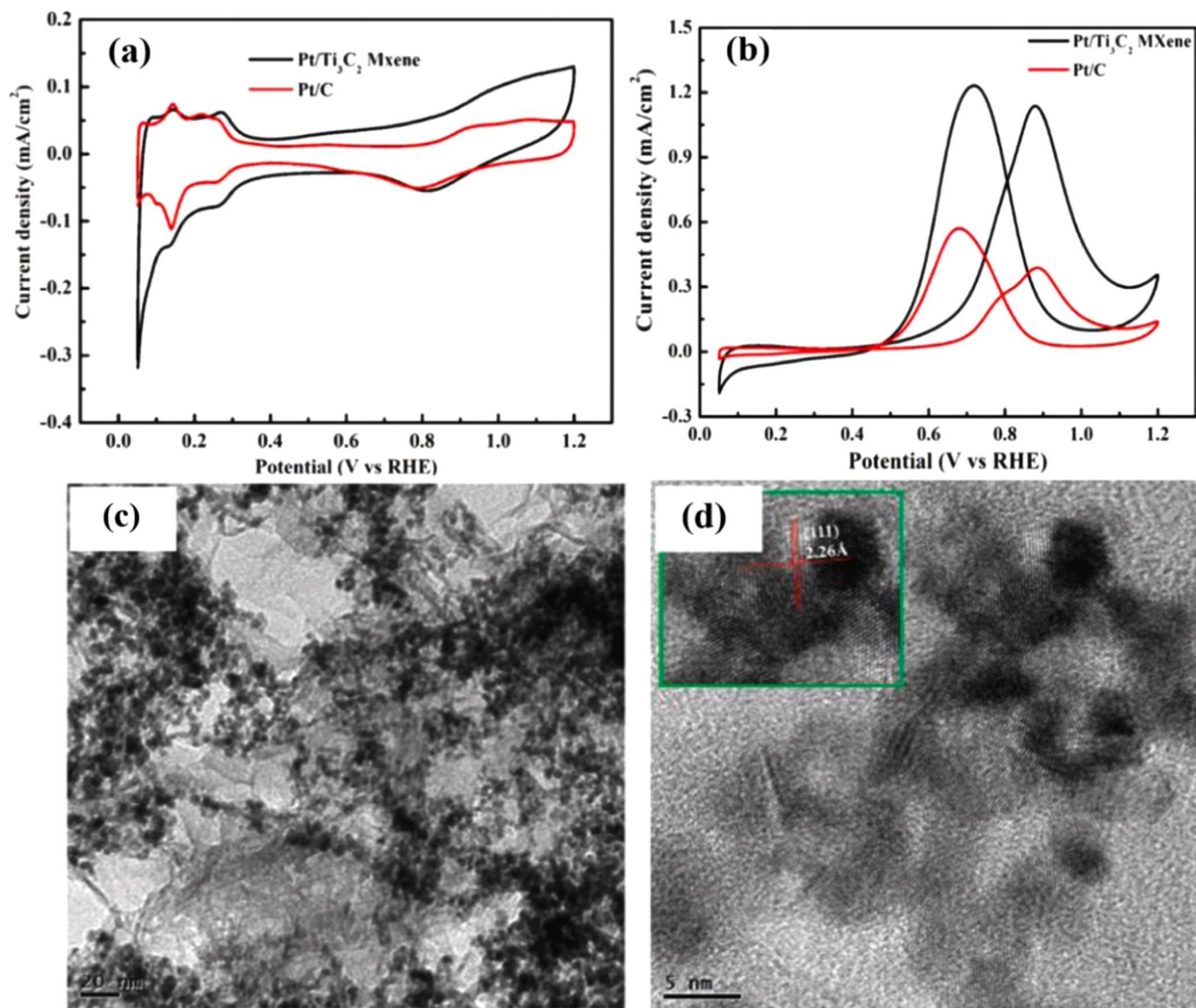


Fig. 12. (a) Cyclic voltammogram (CV) curves of Pt/Ti₃C₂T_x MXene and commercial Pt/C in N₂-saturated 0.5 M H₂SO₄ solution, (b) CV curves of MOR on Pt/Ti₃C₂T_x MXene and commercial Pt/C in 0.5 M H₂SO₄ + 0.5 M CH₃OH solution at a scan rate of 50 mV/s, (c) TEM, and (d) HRTEM of Pt/Ti₃C₂T_x MXene surface. Reprinted with permission from [219].

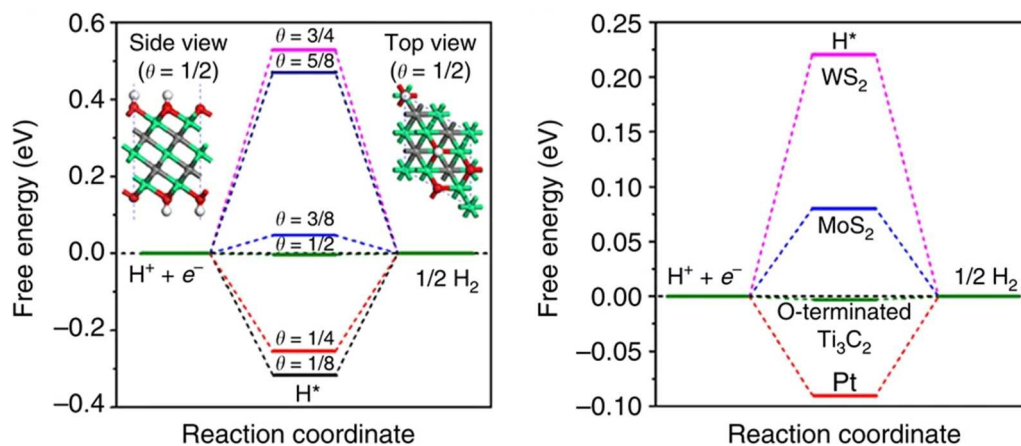


Fig. 13. Calculated free energy for HER, for (a) Ti₃C₂T_x at various H^{*} coverage (1/8, 1/4, 3/8, 1/2, 5/8 and 3/4) and (b) Pt, MoS₂, and WS₂ at 1/2 H^{*} coverage. Reprinted with permission from [260].

found to be irregular and circumstantial. DFT calculations demonstrated that for all possible cases with a bandgap larger than 1.23 eV, the minimum required in order for the water-splitting reaction to occur, Zr_2CO_2 was a promising photocatalyst candidate in water splitting [256].

Utilizing *ab initio* calculations, Guo and coworkers assessed 48 MXenes to unravel their photocatalytic properties. Their outcomes revealed that 2D Zr_2CO_2 and Hf_2CO_2 , whose band gaps and band edges positions substantially met initial requirements for photocatalytic water splitting, possess incredibly high and directionally anisotropic carrier mobility, meaning that they likely facilitate the migration and

separation of photo-generated e^-h^+ pairs. Regarding sunlight absorption, these two MXenes were proved to be effective in optical absorption in the wavelength ranging from 300 to 500 nm. Additionally, these 2D MXenes were potentially stable in a liquid water medium based on *ab initio* molecular dynamic simulations. Eventually, the absorption and decomposition of a water molecule and the formation process of H_2 on concerned MXenes were investigated, which demonstrated to be energetically feasible [85].

The results associated with other research are presented in Table 5, which opens up a novel trend into developing MXene-based HER catalysts or cocatalysts in water-splitting applications.

Table 5

Recent research associated with the development of MXenes as cocatalysts in photocatalytic HER.

MXene cocatalyst	Final catalyst	Sacrificial agent	H_2 production ($\mu\text{mol h}^{-1}\text{g}^{-1}$)	Activity improvement following MXene cocatalyst addition	Ref
$\text{Ti}_3\text{C}_2\text{T}_x$ - monolayer nanosheets	$\text{CdLa}_2\text{S}_4/\text{Ti}_3\text{C}_2\text{T}_x$	0.25 M Na_2SO_3 , 0.35 M Na_2S	11182.4	13.4 times	[262]
	$\text{TiO}_2/\text{Ti}_3\text{C}_2\text{T}_x$	25% methanol	17.8	4 times	[263]
	$\text{g-C}_3\text{N}_4/\text{Ti}_3\text{C}_2\text{T}_x/\text{TiO}_2$	10% triethanolamine	1620.0	2.41 times (compared to $\text{g-C}_3\text{N}_4$)	[264]
	$\text{g-C}_3\text{N}_4/\text{Ti}_3\text{C}_2\text{T}_x$	10% triethanolamine	72.3	10.18 times	[265]
	$\text{CdS}/\text{Ti}_3\text{C}_2\text{T}_x$	10% lactic acid	2407.0	6.68 times	[266]
	P-doped tubular $\text{g-C}_3\text{N}_4/\text{Ti}_3\text{C}_2\text{T}_x$	20% methanol	565.0	3.07 times	[267]
	heptazine-based $\text{g-C}_3\text{N}_4/\text{Ti}_3\text{C}_2\text{T}_x$	10% triethanolamine	4225.0	1.84 times	[268]
	$\text{CuS}/\text{Ti}_3\text{C}_2\text{T}_x$	0.25 M Na_2SO_3 , 0.35 M Na_2S	4.2	1.42 times	[269]
	Black phosphorus/ultrathin $\text{g-C}_3\text{N}_4/\text{Ti}_3\text{C}_2\text{T}_x$	10% triethanolamine	18420.0	19.4 times	[270]
	Protonated $\text{g-C}_3\text{N}_4/\text{Ti}_3\text{C}_2\text{T}_x$ / hollow spheres	10% triethanolamine	982.8	3.5 times	[271]
MXene cocatalyst	Final catalyst	Sacrificial agent	H_2 production ($\mu\text{mol h}^{-1}\text{g}^{-1}$)	Activity improvement following MXene cocatalyst addition	Ref
$\text{Ti}_3\text{C}_2\text{T}_x$ - multilayer nanosheets	$\text{ZnIn}_2\text{S}_5/\text{Ti}_3\text{C}_2\text{T}_x$	0.25 M Na_2SO_3 , 0.35 M Na_2S	2596.8	1.97 times	[272]
	$\text{g-C}_3\text{N}_4/\text{Ti}_3\text{C}_2\text{T}_x$	20% triethanolamine	26.7	2.13 times	[273]
	$\text{TiO}_2/\text{Ti}_3\text{C}_2\text{T}_x$	Ascorbic acid	33.4	NR ^b	[274]
	/amorphous carbon/ Eosin Y				
	$\text{ZnIn}_2\text{S}_4/\text{TiO}_2/\text{Ti}_3\text{C}_2\text{T}_x$	0.25 M Na_2SO_3 , 0.35 M Na_2S -9 H_2O	1185.8	5.61 times (compared to ZnIn_2S_4)	[275]
	$\text{ZnS}/\text{Ti}_3\text{C}_2\text{T}_x$ microspheres	25% lactic acid	502.6	4 times	[276]
	$\text{MoS}_2/\text{Ti}_3\text{C}_2\text{T}_x/\text{TiO}_2$	Triethanolamine	6425.3	NR ^b	[277]
	$\text{Ti}_3\text{C}_2\text{T}_x(\text{TiO}_2)$	20% lactic acid	8470.0	3.06 times	[278]
	@ CdS/MoS_2				
	Black phosphorus/ $\text{TiO}_2/\text{Ti}_3\text{C}_2\text{T}_x$	25% triethanolamine	684.5	NR ^b	[279]
	$\text{g-C}_3\text{N}_4/\text{Ti}_3\text{C}_2\text{T}_x$	10% triethanolamine	88.0	NR ^b	[280]
	O-doped $\text{g-C}_3\text{N}_4/\text{Ti}_3\text{C}_2\text{T}_x$	Triethanolamine	25124.0	1.82 times	[281]
	$\text{BiOBr}/\text{Ti}_3\text{C}_2\text{T}_x$	0.25 M aqueous methanol	1.3	3.88 times	[282]
	$\text{WS}_2/\text{TiO}_2/\text{Ti}_3\text{C}_2\text{T}_x$	15% acetone, 5% triethanolamine	3409.8	NR ^b	[283]
MXene cocatalyst	Final catalyst	Sacrificial agent	H_2 production ($\mu\text{mol h}^{-1}\text{g}^{-1}$)	Activity improvement following MXene cocatalyst addition	Ref
$\text{Ti}_3\text{C}_2\text{T}_x$ - few layered nanosheets	$\text{ZnIn}_2\text{S}_4/\text{Ti}_3\text{C}_2\text{T}_x$	10% triethanolamine	3475.0	6.6 times	[284]
	$\text{SnNb}_2\text{O}_6/\text{Ti}_3\text{C}_2\text{T}_x$	20% methanol	43.8	1.95 times	[285]
$\text{Ti}_3\text{C}_2\text{T}_x$ quantum dots	$\text{BiVO}_4/\text{ZnIn}_2\text{S}_4/\text{Ti}_3\text{C}_2\text{T}_x$	NR ^a	102.7	≈ 1.42 times	[286]
	$\text{g-C}_3\text{N}_4/\text{Ti}_3\text{C}_2\text{T}_x$	15% triethanolamine	5111.8	25.97 times	[287]
$\text{Ti}_3\text{C}_2\text{T}_x$ nanoparticles	$\text{CdS}-\text{Ti}_3\text{C}_2\text{T}_x$ cauliflower-like submicron spheres	18% lactic acid	14342.0	136.59 times	[260]
	$\text{g-C}_3\text{N}_4/\text{Ti}_3\text{C}_2\text{T}_x/\text{Pt}$	10% triethanolamine	5100.0	5 times	[288]
	$\text{UiO}-66-\text{NH}_2/\text{Ti}_3\text{C}_2\text{T}_x$	0.1 M Na_2S , 0.1 M Na_2SO_3	204.0	7.96 times	[289]
	$\text{g-C}_3\text{N}_4/\text{Mo}_2\text{C}$ nanorods	10% triethanolamine	507.0	2.34 times	[290]
Mo_2C - nanoparticles ($\text{Mo}_2\text{C}/\text{C}$)	$\text{Mo}_2\text{C}/\text{C}/\text{g-C}_3\text{N}_4$	10% triethanolamine	2269.5	333.74 times	[291]
Mo_2C - nanosheets	$\text{Mo}_2\text{C}/\text{CdS}$	20% lactic acid	7700.0	16.38 times	[292]

^a $\text{g-C}_3\text{N}_4$ = graphitic carbon nitride

^b NR = Not reported

3.2. Carbon dioxide reduction reaction

Massive CO₂ emissions resulting from burning high levels of fossil fuels have been among the threatening problems of industrialization in the past century. As such, there is strong interest in converting this gas, via CO₂RR, to high value-added and clean products (CO, CH₄, CH₃OH, etc.) [293,294]. In this regard, photocatalytic reactions have shown promise in mimicking the natural photosynthesis of green plants, driving CO₂ conversion via solar radiation [295].

Recently, photocatalysts, such as metal oxides [296], nitrides [297], and sulfides [298], have been found to possess photocatalytic activity toward CO₂RR. However, these materials suffer from low efficiency in practical applications due to their poor ability to hinder the recombination of electron-hole pairs during their transfer [299]. To address this problem, noble metals (e.g., Au, Pd, Pt, Ru) have been combined with conventional catalysts to boost CO₂RR efficiency. However, the high cost of this strategy has hindered the industrial-scale use of these catalysts. Hence, affordable and efficient catalysts or cocatalysts to meet industrial demands are needed [300].

Solar-driven MXenes have attracted substantial interest as emerging CO₂RR photocatalysts owing to their improved performance in the separation and transformation of charge carriers. Several review articles have comprehensively investigated the potential of MXenes in CO₂RR for producing environmentally friendly products [249,253,301–303]. As mentioned earlier, MXene-based photocatalysts promote the conversion of CO₂ to substances like CO, CH₃OH, and CH₄. CO₂RR proceeds within two main steps: 1) the incident light collides onto the photocatalyst surface and separates electrons (e⁻) and holes (h⁺) only if the energy of the incident light is equal to or greater than the bandgap of the photocatalyst, thereby transferring e⁻ to the photocatalytic surface, 2) CO₂ captures e⁻ and protons (H⁺), and corresponding products are generated. Simultaneously, water is oxidized into O₂ (Fig. 14) [304].

The reactions by which CO₂ is converted into CH₃OH, CO, and CH₄ are as follows [305]:



Several studies have demonstrated the paramount influence of MXenes on CO₂ reduction. As an illustration, Chen *et al.* [306] investigated the in-situ growth of TiO₂ on Ti₃C₂T_x, which established a Schottky junction between these materials. They discovered that the optimal TiO₂/Ti₃C₂T_x structure resulted in 2.8 and 4 times higher production rates than pristine TiO₂ for CO and CH₄, respectively. This improvement in CO₂RR performance was due to forming an intimate

interface between TiO₂ and Ti₃C₂T_x via Schottky heterojunctions, which encouraged the separation of e⁻-h⁺ pairs. It seems Schottky heterojunctions have more positive effects on the e⁻-h⁺ separation and electron mobility than when MXene and the second substance are mechanically mixed. In a study carried out by Wang *et al.* [307], a heterojunction 2D/2D was constructed by combining La₂Ti₂O₇ and few-layered Ti₃C₂T_x. The outcomes indicated that the La₂Ti₂O₇/Ti₃C₂T_x possessed Schottky heterojunctions and yielded more CO and CH₄, whose production rates were 4.6 and 11.4 times more than the La₂Ti₂O₇/Ti₃C₂T_x fabricated by a facile mechanical mixing method. Zhang *et al.* [308] prepared a Cu₂O/Ti₃C₂T_x heterojunction composite through an in situ hydrothermal growth procedure with 2, 5, 10, 20, and 30 percent of Ti₃C₂T_x. According to their results, the as-prepared composite with 10% Ti₃C₂T_x exhibited the highest photocatalytic CO₂RR performance, with 3.1 and 4.0 times greater CO and CH₄ yield rates (17.55 μmol·g⁻¹·h⁻¹ and 0.96 μmol·g⁻¹·h⁻¹, respectively) than pristine Cu₂O (5.73 μmol·g⁻¹·h⁻¹ for CO and 0.24 μmol·g⁻¹·h⁻¹ for CH₄). This CO₂RR enhancement was attributed to the formation of a heterojunction contact surface between Cu₂O and Ti₃C₂T_x, which improved the separation of photogenerated e⁻-h⁺ pairs. From prior research, Table 6 represents the effect of MXene incorporation into photocatalysts on overall CO₂RR yield rate or yield.

3.3. Nitrogen reduction reaction

Ammonia (NH₃) is widely used in many applications, including refrigeration [324], textiles [325], plastics, pesticides, and dyes [326]. As mentioned, NH₃ is usually produced industrially using the Haber-Bosch (HB) process, which requires harsh processing conditions [327]. These extreme conditions are due to the high dissociation energy of the N₂ triple bond, the thermodynamically forbidden addition of the H atom to N₂, and the high chemical stability of N₂ [328]. Moreover, the HB process contributes to CO₂ generation [329], which has motivated the research community to develop sustainable alternative processes.

Photocatalytic N₂ reduction has been found to be an attractive way of NH₃ fabrication. Recently, various photocatalysts have been exploited as potential NRR photocatalysts for driving solar energy and promoting N₂ conversion [330]. There are fundamental differences between the HB process and photocatalytically-based NRR regarding their hydrogen source, processing conditions, catalysts, and energy source (Table 7) [331]. Photocatalyst-assisted NRRs follow these three steps: (1) Solar radiation is absorbed by the photocatalyst and excites electrons (e⁻) to move from the VB to the CB provided that the visible light energy (hν) is greater than the forbidden band width (E_g) of the catalyst, leaving positively-charged holes (h⁺) in the VB. (2) Some e⁻-h⁺ pairs recombine, and the rest diffuse into the catalyst surface. (3) Electrons react with H⁺ and N₂ to produce NH₃, and holes combine with H₂O to yield O₂ and H⁺ (Fig. 15) [332].

Like electrocatalytic NRR, the photocatalytic reaction proceeds via four well-defined pathways: dissociative, distal associative, alternative associative, and enzymatic (Fig. 10) [330,331]. Concerning N₂ immobilization and activation, some roadblocks in NRR involve the slow kinetics of N₂ reduction due to the six-electron transfer procedure, the combination of e⁻-h⁺ pairs, the potential reduction, and the light absorption range. Consequently, using an appropriate photocatalyst with acceptable VB-CB potentials is imperative for the suitable activation of N₂ and reduction to NH₃ [333]. Potential NRR photocatalysts have been extensively investigated, encompassing single atoms [334], transition metal oxides [335], transition metal sulfides [336], bismuth oxide (oxyhalides) [337], graphitic C₃N₄ [338,339], and bionic materials [340].

MXenes have attracted paramount interest in N₂ fixation during the past decade. The attractiveness of MXenes in photocatalytic reaction applications is due to their high surface area, which provides extensive active sites for concerned reactants, and the creation of the Schottky barrier to hamper the recombination of charge carriers [341]. In view of the photocatalytic activity, MXenes favor photocatalytic NRR

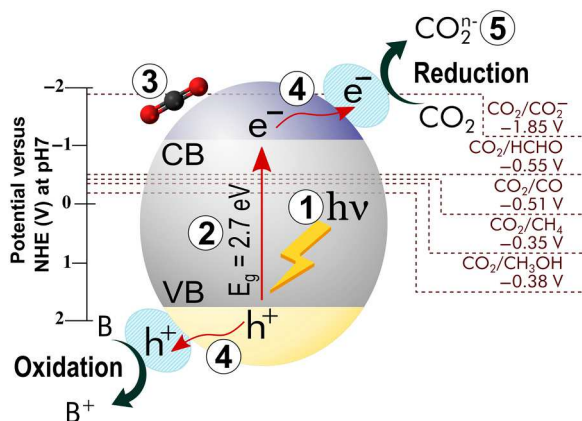


Fig. 14. Schematic illustration of the mechanism of photocatalytically-driven CO₂RR. Reprinted with permission from [304].

Table 6
A summary of the CO₂RR performance of various photocatalysts after adding a MXene component.

Photocatalyst	Product (s)	Light source	Yield rate or yield	Ref
Ti ₃ C ₂ T _x	CH ₄ and CO	300 W high-pressure Xe lamp	CH ₄ , 0.88 μmol·g ⁻¹ ·h ⁻¹ CO, 3.10 μmol·g ⁻¹ ·h ⁻¹	[309]
g-C ₃ N ₄ /Ti ₃ C ₂ T _x			CH ₄ , 2.12 μmol·g ⁻¹ ·h ⁻¹ CO, 3.98 μmol·g ⁻¹ ·h ⁻¹	
TiO ₂	CH ₄	300 W Xe lamp	~ 0.059 μmol·h ⁻¹	[310]
TiO ₂ /Ti ₃ C ₂ T _x g-C ₃ N ₄	CH ₄ and CO	Xe lamp	0.220 μmol·h ⁻¹ CH ₄ , 0.20 μmol·g ⁻¹ ·h ⁻¹ CO, 0.79 μmol·g ⁻¹ ·h ⁻¹	[311]
ZnO			CH ₄ , 0.17 μmol·g ⁻¹ ·h ⁻¹ CO, 0.52 μmol·g ⁻¹ ·h ⁻¹	
g-C ₃ N ₄ /ZnO			CH ₄ , 0.27 μmol·g ⁻¹ ·h ⁻¹ CO, 1.41 μmol·g ⁻¹ ·h ⁻¹	
g-C ₃ N ₄ /ZnO/Ti ₃ C ₂ T _x			CH ₄ , 0.26 μmol·g ⁻¹ ·h ⁻¹ CO, 6.41 μmol·g ⁻¹ ·h ⁻¹	
PCN ^a	CH ₄ and CO	35 W HID Car lamp	CH ₄ , 23.4 μmol·g ⁻¹ ·h ⁻¹ CO, 63.5 μmol·g ⁻¹ ·h ⁻¹	[312]
TiC-48/PCN			CH ₄ , 157.1 μmol·g ⁻¹ ·h ⁻¹ CO, 634.8 μmol·g ⁻¹ ·h ⁻¹	
Photocatalyst	Product (s)	Light source	Yield rate or yield	Ref
Ni/Nb ₂ O ₅	CH ₄	300 W Xe arc lamp	12.9 mmol·g ⁻¹ ·h ⁻¹	[313]
Ni/Nb ₂ CT _x			72.5 mmol·g ⁻¹ ·h ⁻¹	
CN BCN ^b Ti ₃ C ₂ T _x /BCN ^b	CO	Visible light	4.47 μmol·g ⁻¹ ·h ⁻¹ 6.42 μmol·g ⁻¹ ·h ⁻¹ 14.40 μmol·g ⁻¹ ·h ⁻¹	[314]
TiO ₂ (P25)	CO and CH ₄	300 W Xe lamp	CH ₄ , ~ 0.06 μmol·g ⁻¹ ·h ⁻¹ CO ~ 3.91 μmol·g ⁻¹ ·h ⁻¹	[315]
TiO ₂ (P25)/ Ti ₃ C ₂ OH			CH ₄ , 16.61 μmol·g ⁻¹ ·h ⁻¹ CO, 11.74 μmol·g ⁻¹ ·h ⁻¹	
g-C ₃ N ₄	CO and CH ₄	300 W Xe lamp	CH ₄ , NR ^d	[316]
g-C ₃ N ₄ /Ti ₃ C ₂ OH			CO, 1.88 μmol·g ⁻¹ ·h ⁻¹ CH ₄ , NR ^d CO, 11.21 μmol·g ⁻¹ ·h ⁻¹	
Bi ₂ WO ₆	CH ₄ and CH ₃ OH	300 W Xe lamp	CH ₄ , 0.39 μmol·g ⁻¹ ·h ⁻¹ CH ₃ OH, 0.1 μmol·g ⁻¹ ·h ⁻¹	[317]
Bi ₂ WO ₆ / Ti ₃ C ₂ T _x			CH ₄ , 1.78 μmol·g ⁻¹ ·h ⁻¹ CH ₃ OH, 0.44 μmol·g ⁻¹ ·h ⁻¹	
Cu ₂ O NWs/Cu	CH ₃ OH	300 W Xe lamp	3.12 ppm·cm ⁻² ·h ⁻¹	[318]
Cu ₂ O/Ti ₃ C ₂ T _x Sheets/Cu			11.98 ppm·cm ⁻² ·h ⁻¹	
Cu ₂ O/Ti ₃ C ₂ T _x QD ^c /Cu			25.77 ppm·cm ⁻² ·h ⁻¹	

Photocatalyst	Product (s)	Light source	Yield rate or yield	Ref
NiAl-LDH	CO	300 W Xe lamp	~ 247.5 μmol·g ⁻¹ ·h ⁻¹	[319]
Ni-LDH/Ti ₃ C ₂ T _x			2128.46 μmol·g ⁻¹ ·h ⁻¹	
TiO ₂	CH ₄ and CO	300 W Xe lamp	CH ₄ , <0.15 μmol·g ⁻¹ ·h ⁻¹ CO, <1.46 μmol·g ⁻¹ ·h ⁻¹	[320]
g-C ₃ N ₄			CH ₄ , NR ^d CO, <1.46 μmol·g ⁻¹ ·h ⁻¹	
TiO ₂ /g-C ₃ N ₄			CH ₄ , NR ^d CO, 3.14 μmol·g ⁻¹ ·h ⁻¹	
TiO ₂ /g-C ₃ N ₄ /Ti ₃ C ₂ T _x			CH ₄ , 1.20 μmol·g ⁻¹ ·h ⁻¹ CO, 4.39 μmol·g ⁻¹ ·h ⁻¹	
Photocatalyst	Product (s)	Light source	Yield rate or yield	Ref
TiO ₂	CO and CH ₄	300 W Xe lamp	CH ₄ , < 0.96 μmol·g ⁻¹ ·h ⁻¹ CO, < 4.86 μmol·g ⁻¹ ·h ⁻¹	[321]
Ru-Ti ₃ CN-TiO ₂			CH ₄ , 8.97 μmol·g ⁻¹ ·h ⁻¹ CO, 99.58 μmol·g ⁻¹ ·h ⁻¹	
Cd _{0.2} Zn _{0.8} S	CO and CH ₄	300 W Xe lamp	CH ₄ , ~ 0.95 μmol·g ⁻¹ ·h ⁻¹ CO ~ 0.8 μmol·g ⁻¹ ·h ⁻¹	[322]
Cd _{0.2} Zn _{0.8} S@Ti ₃ C ₂ T _x			CH ₄ , 3.51 μmol·g ⁻¹ ·h ⁻¹ CO, 3.31 μmol·g ⁻¹ ·h ⁻¹	
Bi ₂ O ₃ SiO ₃	CO and CH ₃ OH	300 W Xe lamp	CH ₃ OH, 1.80 μmol·g ⁻¹ ·h ⁻¹ CO, 3.45 μmol·g ⁻¹ ·h ⁻¹	[323]
Bi ₂ O ₃ SiO ₃ /Ti ₃ C ₂ T _x			CH ₃ OH, 2.07 μmol·g ⁻¹ ·h ⁻¹ CO, 17.82 μmol·g ⁻¹ ·h ⁻¹	

^a PCN = porous g-C₃N₄
^b Boron- doped g-C₃N₄, ^c: Ti₂O/C = produced by Ti₃C₂T_x calcination
^d NR= not reported
^e QD: quantum dot.

Table 7
The differences between the HB process and photocatalytic nitrogen reduction. Reprinted with permission from [331].

	HB process	Photocatalytic nitrogen reduction
Hydrogen source	Natural gas	Water
Catalysts	Iron	Semiconductors
Temperature	400–500 °C	Ambient temperature
Pressure	200 atm	1 atm
Energy source	Fossil fuel	Solar energy

manufacturing NH₃ through an environmentally friendly process. In this respect, several reviews have described the promising contributions of photocatalytic MXenes and their recent developments in photocatalytic NRR [301,342–344]. However, very few articles have been published in this field since it is still in its infancy. To mention in a study by Li *et al.* in 2022 [345], an ultrasonicated Ti₃C₂T_x MXene doped by tungsten (W) atoms (W/Ti₃C₂T_x-U) with regard to its nitrogen photo fixation. The outcomes indicated that bare Ti₃C₂T_x-U and W/Ti₃C₂T_x-U resulted in an NH₃ yield rates of 14.5 and 227.5 μmol·g⁻¹·h⁻¹, respectively. The better efficiency of W/Ti₃C₂T_x-U than Ti₃C₂T_x-U was associated with active sites created by W, which further promoted electron transfer and N₂

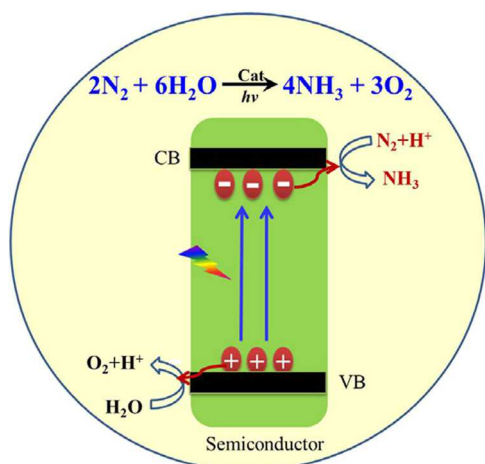


Fig. 15. A general schematic of nitrogen reduction via photocatalysts. Reprinted with permission from [332].

adsorption. In another study, Jiang *et al.* [346] synthesized a 2D MXene-derived Nb₂O₅/C/Nb₂C/g-C₃N₄ heterojunction via immobilizing Nb₂O₅ on Nb₂C and subsequently, the in-situ formation of g-C₃N₄ nanosheets on Nb₂O₅/C/Nb₂C. The prepared composite showed a 9.1 times greater NH₃ production rate of 0.365 mmol.g⁻¹.h⁻¹ than that of MXene-derived Nb₂O₅/g-C₃N₄. This enhancement was attributed to the close contact between Nb₂O₅ and Nb₂C and the Schottky junction formed at the Nb₂O₅/Nb₂C interface, assisting charge transfer and boosting the overall N₂ fixation efficiency. Chang *et al.* [347] fabricated a reduced Ti₃C₂T_x MXene embedded with Au nanoparticles (r-Ti₃C₂T_x/Au). r-Ti₃C₂T_x provided more Ti active sites, which can facilitate N₂ adsorption and activation. Moreover, Au nanoparticles donated plasmonic hot electrons to promote the reduction of already activated N₂ molecules. The synthesized r-Ti₃C₂T_x/Au composite demonstrated an NH₄⁺ production rate of 12.4 μmol.g⁻¹.h⁻¹ under visible light, approximately 5.9 and 10.3 times those of Ti₃C₂T_x/Au and r-Ti₃C₂T_x, respectively. This effect obviously indicates the synergic influences of increased Ti active sites and accessibility to electrons. Other research regarding the application of MXenes in NRR is briefly represented in Table 8.

Table 8

The efficiency of MXene-based photocatalysts in photo-induced N₂ reduction. A 300 W xenon lamp was used in all cases.

Photocatalysts	NH ₃ yield rate	NRR activity improvement following the incorporation of MXene	Ref
Ti ₃ C ₂ T _x /TiO ₂	422.0 μmol.g ⁻¹ .h ⁻¹	NR ^a	[348]
1D/2D CdS nanorod@Ti ₃ C ₂ T _x	293.1 μmol.L ⁻¹ .h ⁻¹	NR ^a	[349]
0D/2D AgInS ₂ /Ti ₃ C ₂ T _x	38.8 μmol.g ⁻¹ .h ⁻¹	19.4 times	[350]
Bi ₄ O ₅ Br ₂ /Ti ₃ C ₂ T _x	277.7 μmol.g ⁻¹ .h ⁻¹	5 times	[351]
Ti ₃ C ₂ T _x /CuZnInS	45.6 μmol.g ⁻¹ .h ⁻¹	2 times	[352]
BiOBr/Ti ₃ C ₂ T _x	234.6 μmol.g ⁻¹ .h ⁻¹	48.8 times	[353]
Ti ₃ C ₂ T _x /TiO ₂ /Co	69.2 μmol.g ⁻¹ .h ⁻¹	1.4 times	[354]
Ti ₃ C ₂ T _x /TiO ₂	50.0 μmol.g ⁻¹ .h ⁻¹	1.8 times	[354]
r-Ti ₃ C ₂ T _x QDs/g-C ₃ N ₄	328.9 μmol.g ⁻¹ .h ⁻¹	NR ^a	[355]

^a NR = not reported

3.4. Water pollutant degradation

Organic matter released from facilities, chemical plants, transportation systems, and refineries enter lakes, seas, oceans, and other aquatic milieu, posing a severe threat to ecosystems and human health [356]. Hence, it is of great importance to develop materials to remove water pollutants through various water treatment routes, including adsorption [357], membrane separation [358], and catalytic reactions. However, these methods suffer from low contaminant removal efficacy, rising premiums, and the emission of toxic by-products [359]. Motivated by these, in the past few years, emerging advanced oxidation processes (AOPs), which include electrolysis, ozonation, and photocatalysis, have been introduced to purify aquatic environments [360]. Solar light-driven pollutant degradation is among the most emerging techniques to alleviate water pollution. In a typical photo-assisted degradation, when light collides with the catalyst surface, the VB electrons are excited and transferred to the CB, forming holes in the corresponding CB. Subsequently, these electron-hole pairs bring about redox reactions in which electrons reduce existing O₂ molecules, and holes function as active sites to oxidize H₂O molecules, thereby creating O₂⁻ and OH⁺ reactive species. Lastly, these will interact with pollutants and convert them to benign products. The diagrammatic illustration of a typical photo-induced pollutant degradation is depicted in Fig. 16 [361].

Photocatalysts fall into multifarious categories, most of which were mentioned in the prior section. Nevertheless, these catalysts represent vital challenges, such as charge carrier recombination and low chemical stability, diminishing the overall performance of photocatalytic pollutant degradation. Accordingly, producing highly efficient materials as alternatives to traditional photocatalysts is crucial [362].

MXenes with high surface area and negatively charged surface enable the intercalation of positively charged cations (e.g., Na⁺, K⁺, and Li⁺) and organic molecules (e.g., dimethyl sulfoxide (DMSO) and urea) in between MXenes layers, thereby promoting the removal of contaminants from water [363]. Moreover, with their surface functional groups (e.g., F, O, and OH), MXenes can be potential hosts for other catalysts to form potent photocatalysts for the spontaneous depletion of contaminants [364]. So, MXenes are usually employed with other materials in the form of composites because MXenes alone lack proper semi-conducting characteristics [365]. Several investigations have been conducted on the performance of MXenes incorporating photocatalysts toward eliminating a wide array of contaminants. For example, in a study by Shahzad and coworkers [366], a hybrid Ti₃C₂T_x/TiO₂ photocatalyst was fabricated via a facile hydrothermal method. The heterostructure of the as-synthesized photocatalyst was attained by the Schottky junction formed between the Ti₃C₂T_x and TiO₂ interfaces. The fabricated photocatalyst was investigated regarding its potential photocatalytic application in the degradation of antiepileptic drug carbamazepine (CBZ). The resulting degradation stage rate of Ti₃C₂T_x/TiO₂ (10.0 mg) was 0.0304 min⁻¹ under ultraviolet radiation, higher than that under solar light (Fig. 17a and b). Furthermore, the percent decomposition of CBZ by pristine Ti₃C₂T_x and Ti₃C₂T_x/TiO₂ was 60% and 98.67%, respectively, clearly showcasing the effect of TiO₂ incorporation. The mechanism through which the degradation occurs is illustrated in Fig. 17(c). As this figure shows, when light radiates onto the Ti₃C₂T_x/TiO₂ surface, the VB electrons (e⁻) are excited and leave the VB to CB, forming respective holes (h⁺) in CB. The e⁻-h⁺ pairs then react with dissolved oxygen to generate reactive •OH radicals, which decompose CBZ to produce CO₂ and H₂O. The remarkable photocatalytic activity of Ti₃C₂T_x/TiO₂ was ascribed to the extra e⁻-h⁺ pairs generated by {0 0 1} facets of TiO₂ along with the formation of the Schottky junction. In another research, Chen *et al.* [367] constructed bismuth oxychloride (BiOCl)/Ti₃C₂T_x MXene heterostructures through a simple electrostatic self-assembly pathway (Fig. 18a). This MXene-based substance resulted in up to 90% photodegradation of ciprofloxacin (CIP), a fluoroquinolone antibiotic, in only 30 min under sunlight irradiation. This enhancement in degradation was correlated with the

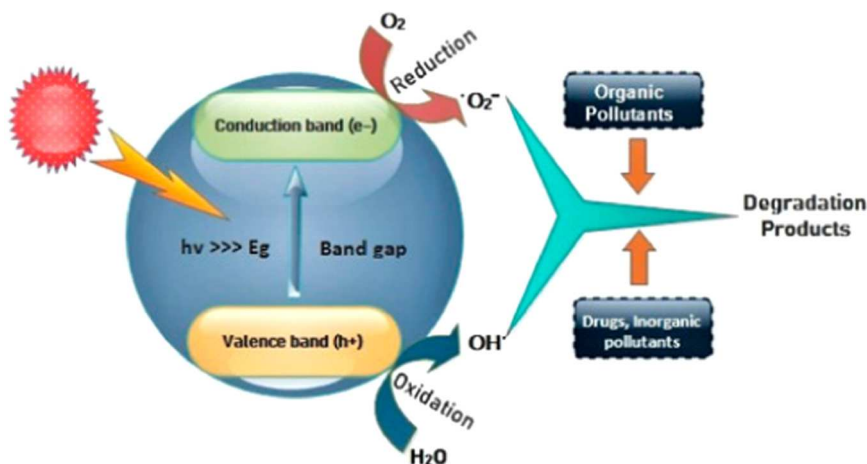


Fig. 16. The diagrammatic representation of a general solar light-assisted pollutants degradation Reprinted with permission from [361].

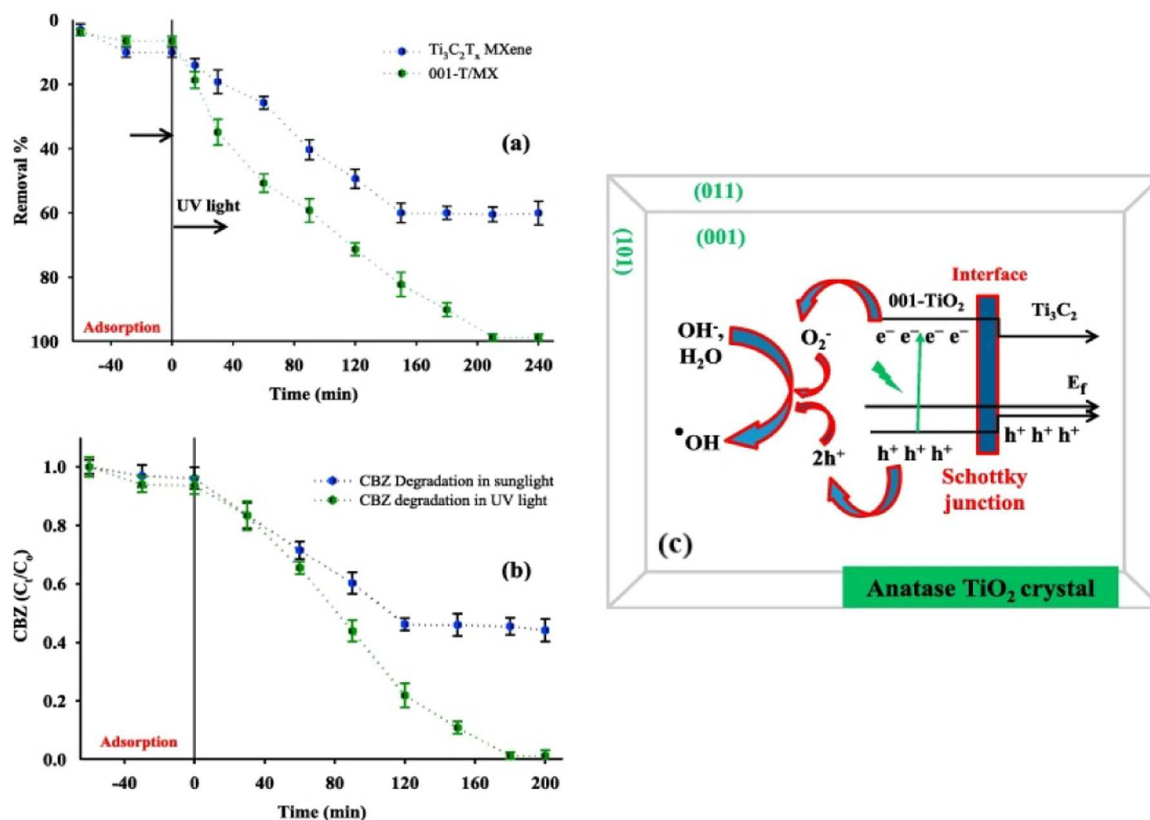


Fig. 17. (a) Comparison between pristine Ti₃C₂T_x and Ti₃C₂T_x/TiO₂ photocatalysts for the degradation capacity of CBZ. (b) The degradation of CBZ under UV and solar light irradiation utilizing Ti₃C₂T_x/TiO₂ photocatalyst. (c) Schematic illustration of CBZ degradation mechanism by Ti₃C₂T_x/TiO₂. Reprinted with permission from [366].

hindrance of e^-h^+ pairs recombination and the improved light absorption capacity. The influence of adding different amounts of Ti₃C₂T_x on the photocatalytic performance of as-prepared catalysts is depicted in Fig. 18(b). First, a 30 min of physical blending between BiOCl and Ti₃C₂T_x occurred. Subsequently, the stimulated sunlight source was switched on.

Grzegórska *et al.* [368] prepared a hybrid Zn/Ti LDH photocatalyst integrated with Ti₃C₂T_x MXene. They assessed its improved ability for acetaminophen and ibuprofen, both commonly present in the aquatic milieu. They discovered that the LDH/MXene sample containing 2.5%wt of MXene reached the highest degradation of 100% (within 40 min) and 99.7% (within 60 min) for acetaminophen and ibuprofen, respectively

(Fig. 19a and b). With regard to the activity of reactive species, O₂^{-•} had the main contribution to photocatalytic degradation of acetaminophen, whereas •OH and h⁺ were more reactive toward ibuprofen. More importantly, characterization analyses revealed the outstanding stability and reusability of the LDH/Ti₃C₂T_x photocatalyst after four subsequent cycles of degradation (Fig. 19c). After the fourth cycle, the photocatalytic efficacy of the synthesized Zn/Ti LDH-Ti₃C₂T_x in acetaminophen degradation remained 100% within 40 min. In another study, tetracycline hydrochloride (TC-HCl), a common antibiotic found in pharmaceutical wastewater, was degraded by BiOBr/Ti₃C₂T_x/g-C₃N₄. Their outcomes indicated 99% degradation of TC-HCl within 30 min, which was 12 times higher than the degradation efficacy of pure g-C₃N₄

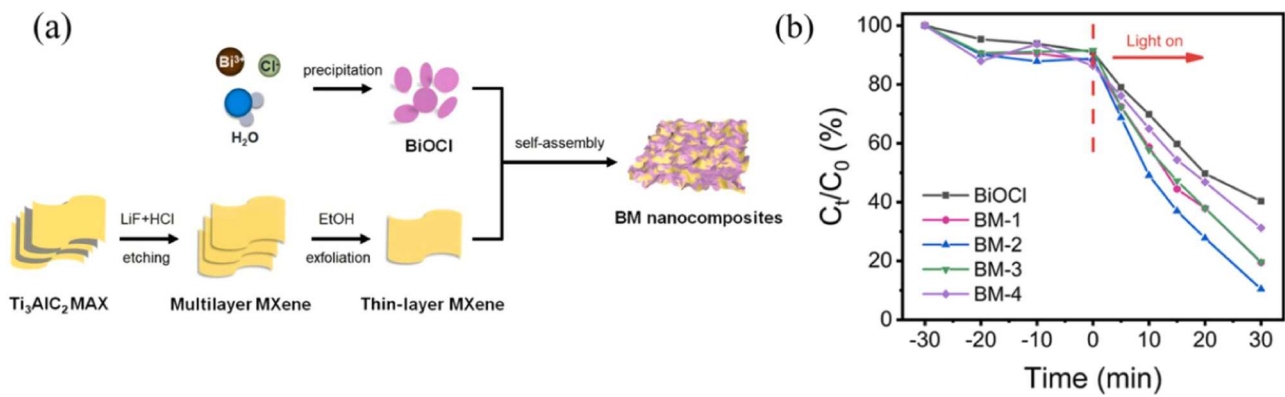


Fig. 18. (a) The preparation route of the $\text{BiOCl}/\text{Ti}_3\text{C}_2\text{T}_x$ photocatalyst via a self-assembly strategy. (b) The photocatalytic activity of $\text{BiOCl}/\text{Ti}_3\text{C}_2\text{T}_x$ in the degradation of CIP. Reprinted with permission from [367].

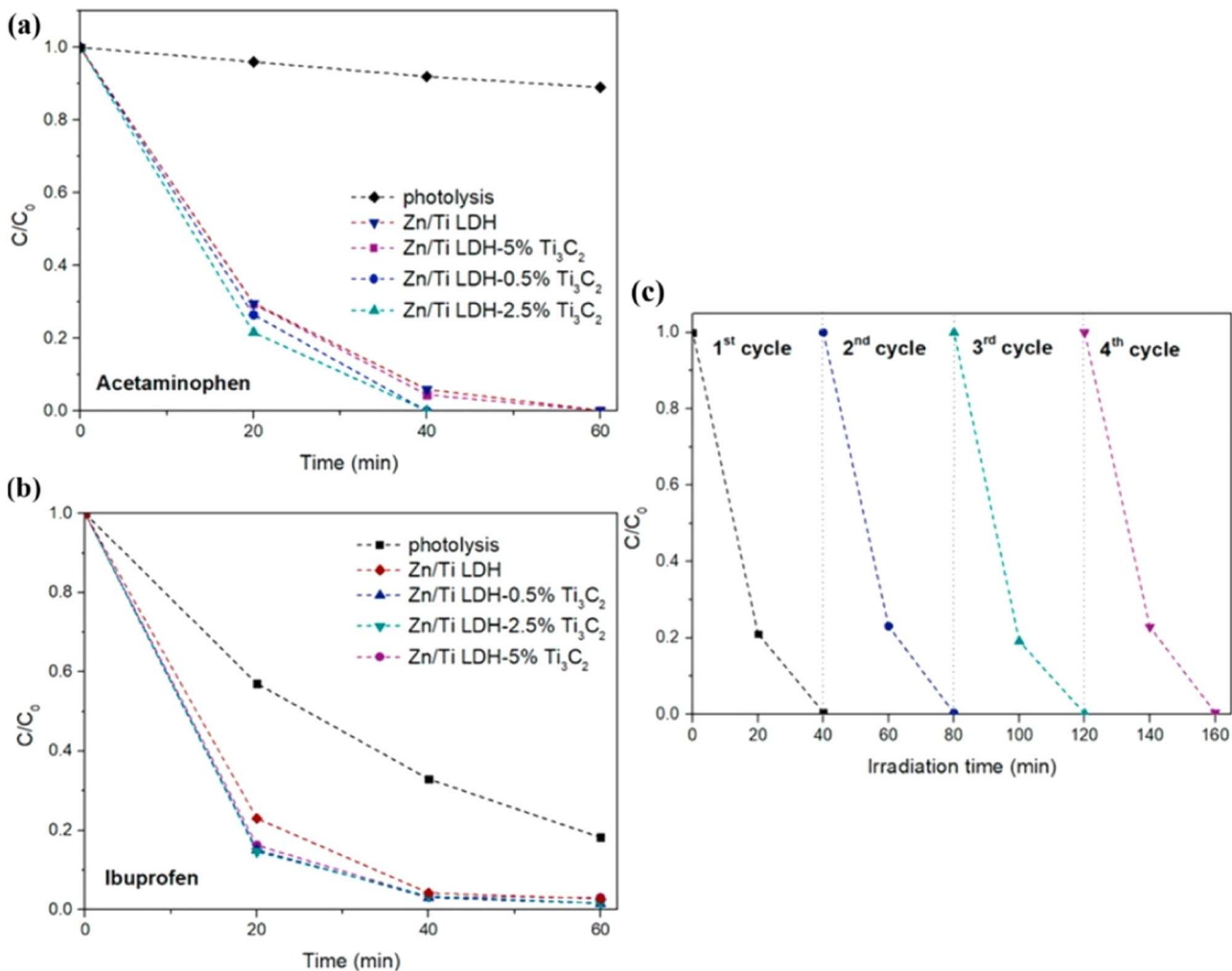


Fig. 19. The performance of Zn/Ti LDH coupled with $\text{Ti}_3\text{C}_2\text{T}_x$ in photocatalytic degradation of (a) acetaminophen and (b) ibuprofen. (c) The stability of fabricated Zn/Ti LDH- $\text{Ti}_3\text{C}_2\text{T}_x$ in acetaminophen degradation after four successive cycles. Reprinted with permission from [368].

(Fig. 20(a)). This improvement was brought about by the increased number of exposed active sites, increased formation of adsorbed oxygen, avoidance of recombination of electron-hole pairs, and efficient production of reactive $\cdot\text{O}_2^-$, h^+ , and $^1\text{O}_2$ (singlet oxygen generated by superoxide radical reactions) [369].

Due to their severe threat to aquatic environments, organic dyes must be removed and degraded via various degradation routes [370].

Fig. 20(b) depicts the MXene-induced photocatalytic degradation of a detrimental organic dye called methylene blue (MB). The MXene used in this research was $\text{Ti}_3\text{C}_2\text{T}_x$ oxidized with TiO_2 and decorated with Ag and Pd NPs. The results showed the superior performance of AgNPs (PdNPs)/ $\text{TiO}_2/\text{Ti}_3\text{C}_2\text{T}_x$ compared to pristine, which was mainly ascribed to the significant role of TiO_2 and Ag(Pd) in augmenting light harvesting, dye adsorption, and charge separation capability [370]. Fig. 20(c)

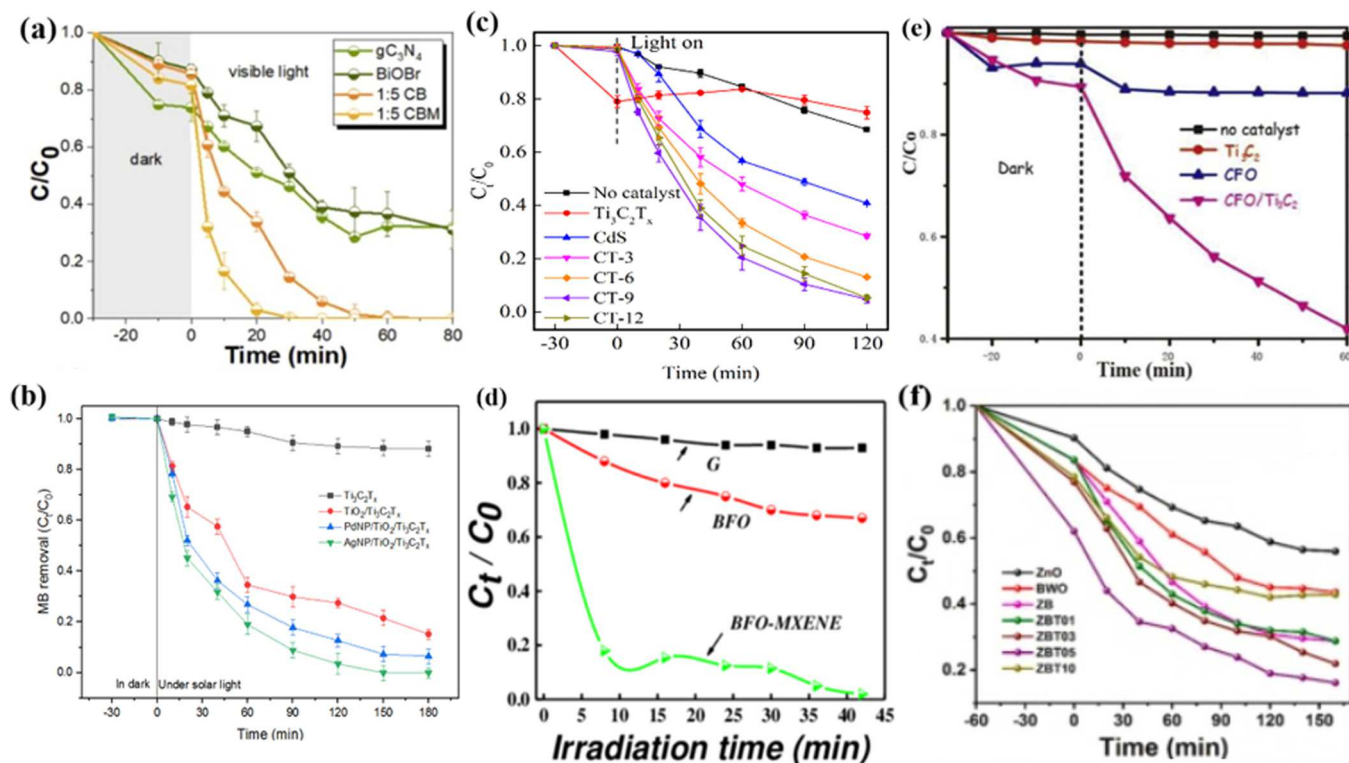


Fig. 20. The photocatalytic degradation of (a) TC-HCl by BiOBr/MXene/g-C₃N₄, (b) MB by AgNPs(PdNPs)/TiO₂/Ti₃C₂T_x, (c) CBZ by CdS QDs/ Ti₃C₂T_x, (d) CR by BiFeO₃/Ti₃C₂T_x, (e) SMZ by CuFe₂O₄/Ti₃C₂T_x, and (f) CFX by ZnO–Bi₂WO₆–Ti₃C₂T_x. (a) reprinted with permission from [369], (b) reprinted with permission from [370], (c) reprinted with permission from [371], (d) reprinted with permission from [372], (e) reprinted with permission from [374], and (f) reprinted with permission from [375].

illustrates the effect of CdS QDs/Ti₃C₂T_x photocatalyst on the degradation of CBZ. In this research, CdS QDs were intimately grafted onto the surface of Ti₃C₂T_x MXene. Therefore, the interface between CdS QDs and Ti₃C₂T_x substantially improved the generation of charge carriers, their separation, and their transfer from CdS. As for the reactive intermediates involved in the removal of CBZ, $\bullet\text{O}_2^-$, H_2O_2 , $^1\text{O}_2$, and $\bullet\text{H}$ were the main active superoxide radicals, with $\bullet\text{O}_2^-$ possessing the primary contribution [371]. In another similar study, Iqbal *et al.* [372] reported the removal of Congo Red (CR) contaminant from water utilizing a nanohybrid system composed of bismuth ferrite nanoparticles with two-dimensional (2D) MXene sheets, namely, the BiFeO₃ (BFO)/Ti₃C₂T_x (MXene) (Fig. 20(d)). 100% of CR was discovered to be degraded from water in 42 min, indicating the paramount effect of the fabricated nanohybrid structure attributed to its light-harvesting ability for photocatalysis. Moreover, the rapid and efficient removing of CR was caused by the low recombination rate of (e^- , h^+) pairs and the large surface area of the nanohybrid. Rhodamine B (RhB) is another water pollutant found to be hazardous to aquatic milieu [373]. To tackle this issue, Liu *et al.* [373] conducted a study on the degradation of RhB by TiO₂/Ti₃C₂T_x MXene. They found that TiO₂/Ti₃C₂T_x can remove RhB from water by 44% in 150 min, which was more effective than Ti₃C₂T_x (30%). This improvement stemmed from better separation of charge carriers and increased light adsorption compared to pristine Ti₃C₂T_x. Cao and coworkers [374] employed CuFe₂O₄/Ti₃C₂T_x MXene hierarchical heterostructures as photocatalysts for improved degradation of Sulfamethazine (SMZ), which causes serious contamination of aquatic media (Fig. 20(e)). Transient surface photovoltage (TPV) spectroscopy was conducted to assess charge carrier lifetimes, indicating that the lifetime of the (e^- , h^+) pair was prolonged by incorporating Ti₃C₂T_x due to the inhibition of charge carrier recombination. Lastly, Sharma *et al.* [375] assessed the photocatalytic degradation of a colorless pharmaceutical pollutant, ciprofloxacin (CFX), using a novel 2D-2D-2D ternary photocatalyst ZnO–Bi₂WO₆–Ti₃C₂T_x. Their results showcased the highest degradation

of CFX, ~77% in 160 min, for a sample containing 5 wt% of Ti₃C₂T_x (Fig. 20(f)). This performance was brought about by the efficient separation of photogenerated charge carriers due to the ternary interface established between individual components.

The results associated with other studies conducted in recent years are represented in Table 9.

4. Other reactions

4.1. Hydrogenation reactions

4.1.1. CO₂ hydrogenation to methanol

As previously mentioned, CO₂ has contributed to climate change substantially, increasing the global temperature during the past few decades. Therefore, CO₂ conversion to non-hazardous substances has attracted much attention in recent decades. Photocatalytically and electrochemically-driven strategies for the conversion of CO₂ were covered in the previous sections. In this regard, DFT calculations have shown that surface termination affects the adsorption energies of reaction intermediates [183].

Catalytic CO₂ reduction to methanol is a clean hydrogenation procedure to reduce the concentration of this gas in the atmosphere. However, most catalysts used for this purpose are not efficient enough to drive CO₂ reduction to methanol. For instance, Cu–ZnO–Al₂O₃ is among the most applicable catalysts for driving the CO₂-to-methanol reaction. Nonetheless, this catalyst is generally ineffective in accelerating this reaction [390]. In another study, Cu/ZrO₂ has been proven efficient in improving CO₂ reduction, although it lacks proper activity and selectivity in industrial deployment [391]. As a result, support and Cu-support interface play crucial roles in catalytic CO₂ hydrogenation. In this respect, Zhou and coworkers [392] developed silica-supported and reducible nanosheets of a Mo₂CT_x MXene to engineer Cu/Mo₂CT_x. H₂ treatment caused the migration of Cu from Cu/SiO₂ to Mo₂CT_x and,

Table 9

Recent studies on the photocatalytic performance of MXene-based materials in contaminant degradation.

Photocatalyst	Pollutant(s)	Light source	Degradation efficiency (%)	Remark(s)	Ref
BiOBr/Ti ₃ C ₂ T _x /g-C ₃ N ₄	TC-HCl	300 W Xenon lamp	99.00	-13 intermediates and possible degradation pathways - the photocatalyst can produce an antibacterial effect following radiation	[369]
CdS QDs/ Ti ₃ C ₂ T _x	CBZ	Simulated solar light	Up to 95.2	- degradation efficiency reached its maximum level after nine cycles of CdS QD deposition. - degradation was progressed via the pseudo-first-order model	[371]
CdS/Ti ₃ C ₂ T _x /TiO ₂	sulfachloropyridazine (SCP)	300 W Xenon lamp	100 for all contaminants	- The catalyst was stable after four consecutive cycles - SCP degradation efficiency had a direct relation with the reaction temperature.	[373]
ZnO/Bi ₂ WO ₆ /Ti ₃ C ₂ T _x	MB RhB ciprofloxacin (CFX)	300 W Xenon lamp	77	- Ti ₃ C ₂ T _x facilitated the separation of e ⁻ -h ⁺ pairs	[375]
Ti ₃ C ₂ T _x /TiO ₂ /Ag	-TC-HCl	300 W Xenon lamp	79.5	- Degradation took place in 15 min under light radiation, followed by 45 min under darkness since the enhanced electron storage caused more degradation activity during darkness	[376]
Bi ₂ WO ₆ /Nb ₂ CT _x	Oxytetracycline (OTC)	Visible light ($\lambda > 420$)	81.4	- Photodegradation rate constant of BN-2 for RhB and MB was 2.8 times and 2 times higher than pristine Bi ₂ WO ₆ , respectively	[377]
	RhB		98.9		
	Methyl orange (MO)		99.1		
	MB		99.2		
Photocatalyst	RhB	Light source	99.8	Remark(s)	Ref
	MB		92.7		
	TC-HCl		83.1		
AgNPs(PdNPs)/TiO ₂ /Ti ₃ C ₂ T _x	MB	UV light	85	- Improved photocatalytic degradation efficiency was ascribed to the formation of anatase TiO ₂ and the plasmonic resonance effect of noble metals, which further enhance charge separation	[370]
BiFeO ₃ /Ti ₃ C ₂ T _x	CR	Visible light	100 for both	- Low e ⁻ -h ⁺ recombination rate according to the photoluminescence spectra - The hybrid photocatalyst had a larger surface area of 147 m ² .g ⁻¹ , conducive to the improved degradation	[372]
TiO ₂ /Ti ₃ C ₂ T _x	Acetaminophen RhB	Visible light ($\lambda \sim 554$ nm)	50	Reusable after five cycles	[373]
CuFe ₂ O ₄ /Ti ₃ C ₂ T _x	SMZ	Visible light	59.4	- Lifetime of photo-induced carriers increased after loading Ti ₃ C ₂ T _x - Semi-stable after three cycles	[374]
Ti ₃ C ₂ T _x /NiFe ₂ O ₄ /V ₂ O ₅	RhB	150 W visible light ($\lambda > 400$ nm)	88.7	- Hydroxyl and superoxide anion radicals played the most crucial roles in photodegradation - Almost complete stability after four cycling runs	[378]
Ti ₃ C ₂ T _x /TiO ₂	perfluorooctanoic acid (PFOA)	UV	100	- Photocatalyst was synthesized through the deep eutectic solvents (DESs) method, which expanded the interlayer space between Ti ₃ C ₂ T _x nanosheets, augmenting the growth of TiO ₂ molecules	[379]
Photocatalyst	Pollutant(s)	Light source	Degradation efficiency (%)	Remark(s)	Ref
Ti ₃ C ₂ T _x /TiO ₂	MB	UV	96.44	-	[380]
BiOI ₃ /Ti ₃ C ₂ T _x	TC-HCl	500 W Xenon lamp	93.4	- Excellent recyclability after the fourth cycle (72.4% of TC-HCl was degraded)	[381]
g-C ₃ N ₄ /Ti ₃ C ₂ T _x /black phosphorus (BP)	Levofloxacin	visible light ($\lambda > 420$ nm)	77.4	- P-bridging effect caused by reactions between the active P atom in the black phosphorus nanosheet and as-fabricated g-C ₃ N ₄ improved photocatalytic degradation efficiency - Extraordinary stability following four successive cycles	[382]
	hydrochloride		43.3		
	4-nitrophenol		99		
Ti ₃ C ₂ QDs/SiC	CIP	300 W Xenon lamp ($\lambda > 420$ nm)	74.6	-	[383]
Ag/g-C ₃ N ₄ /Ti ₃ C ₂ T _x	NO ^a	300 W Xenon lamp ($\lambda > 420$ nm)	99.2	- The incorporation of Ag nanoparticles resulted in the localized surface plasmon resonance, accelerating photo-driven degradation	[384]
Fe ₂ O ₃ /Ti ₃ C ₂ T _x	TC	500 W Xe Lamp	92.1	-	[385]
	RhB		98		
g-C ₃ N ₄ /BiOCl/Ti ₃ C ₂ T _x	TC	visible light ($\lambda > 420$ nm)	97	The photocatalyst was reusable after five consecutive cycles	[386]
Ti ₃ C ₂ T _x /Bi ₄ Ti ₃ O ₁₂	TC-OH	500 W Xe Lamp	100 for all contaminants	High stability after four cycles	[387]
Ti ₃ C ₂ T _x /TiO ₂ /BiOCl	RhB	500 W Xe Lamp	78.36	-	[388]
	MO				
	RhB				
La-doped bismuth ferrite/Ti ₃ C ₂ T _x	CR	500 W Xe Lamp	93	- High stability after four cycles	[389]

^a NO = nitrogen oxide

subsequently, increased Lewis acidic Cu^+ sites, improving the overall methanol formation rate. Their results demonstrated that the optimum synthesized catalyst ($\text{Cu}/\text{MoCT}_x/\text{SiO}_{2-6h}$) possessed a higher intrinsic methanol formation rate than $\text{Cu}/\text{SiO}_{2-2h}$ (2.49 versus $0.41 \text{ g h}^{-1} \text{ g}_{\text{Cu}}^{-1}$), with a methanol selectivity of 52% (Fig. 21a). Furthermore, at the constant CO_2 conversion of 1.0%, the methanol selectivity of $\text{Cu}/\text{MoCT}_x/\text{SiO}_{2-6h}$ was more than that of $\text{Cu}/\text{SiO}_{2-2h}$ (Fig. 21b).

4.1.2. Reverse water-gas shift reaction

The reverse water-gas shift reaction (RWGS) is a pathway for converting hazardous CO_2 to CO (a constituent of syngas), which itself can be further used in methanol synthesis and other procedures. To accelerate this reaction, MXene-based substances are valuable and have shown promise. For example, Salvador *et al.* [393] conducted computational studies, including DFT calculations and kinetic phase diagrams, to verify the capability of MXenes in catalyzing the RWGS reaction. They discovered that CO_2 could be dissociated conveniently on a set of 18 carbides and nitride MXene catalysts with super-low CO_2 dissociation energy (E_b^{dis}) values of 0.14 eV for Ti_2C and below the chemical accuracy of 0.04 eV for Mo_2N . The (E_b^{dis}) on Mo_2C MXene is 0.31, which is suitable for CO_2 facile dissociation. The outcomes indicated that the RWGS catalysis occurs in a two-step process because the hydrogenation step is essential to regenerate the MXene catalysis. When CO_2 is adsorbed on the MXene surface, it becomes O-covered, demanding an additional step to restore the employed catalyst. Hence, surface termination type and concentration influence the catalytic activity of MXenes in CO_2 hydrogenation. H_2 -treatment of MXenes with surface terminations can significantly change their catalytic performance for CO_2 hydrogenation. For example, a T_x -free, Mo-terminated 2D- Mo_2C is catalytically more active than Mo_2CT_x , β - Mo_2C , and $\text{Cu-ZnO-Al}_2\text{O}_3$ [394].

4.1.3. Hydrogenation of nitro derivative compounds

Hydrogenation of nitro-substituted materials into amines is vital in industrial applications. However, selective hydrogenation, meaning targeting a given functional group (in the case of nitro derivatives, $-\text{NO}_2$ group), is formidable, calling for developing novel materials to progress the hydrogenation reaction toward desirable products [395]. Thanks to their chemoselective properties and paramount activity due to the presence of dispersed particles, heterogeneous metal-based catalysts hold promise for selective catalytic hydrogenation of nitro derivatives to fabricate favorable materials [396]. Several reports have been published on the potential application of MXene-based catalysts in the progression of nitro compounds' reduction reactions. For instance, Li and coworkers [397] synthesized functionalized core-shell MXene composites through the layer-by-layer (LBL) self-assembly procedure by amine-containing polyethyleneimine (PEI) and carboxyl-containing polyacrylic acid

(PAA), with the final chemical formula of $\text{MXene-COOH} @ (\text{PEI}/\text{PAA})_n @ \text{AuNPs}$ ("n" denotes the number of shell structures) and for the hydrogenation of 2- and 4-nitrophenol (2- and 4-NP). Their results indicated that the optimum composition $\text{MXene-COOH} @ (\text{PEI}/\text{PAA})_{10} @ \text{AuNPs}$ possessed the best stability and repeatability after nine successive cycles of deployment ($\sim 90\%$ conversion). Fan *et al.* [398] carried out a study in 2018 where PdNPs were uniformly dispersed onto the surface of an $\text{alk-Ti}_3\text{C}_2\text{T}_x$ MXene (alk = alkaline) to fabricate a catalyst for the reduction of 4-NP to 4-aminophenol (4-AP). The well-dispersed PdNPs endowed the catalyst with available active sites to promote the complete conversion and selective hydrogenation of 4-NP to 4-AP in 70 min. Moreover, the resultant catalyst demonstrated no substantial loss in efficiency after seven cycles, showcasing its capability to be a promising candidate for multifarious catalytic reactions. Table 10 summarizes recent research studies on the use of MXene and MAX-based catalysts in the reduction of nitro derivatives.

4.1.4. Furfural hydrogenation

Harnessing novel non-fossil substances is a crucial step to producing fuel in energy areas. Furfural is a bio-based material derived from lignocellulose, which can be employed to manufacture various products through the hydrogenation reaction. In particular, $\sim 62\%$ of this hydrogenation product is furfuryl alcohol, which further converts into tetrahydro furfuryl alcohol (THFA), 2-methylfuran (MF), and 2-methyl-tetrahydrofuran (MTHF) [402]. Naguib *et al.* [403] have reported the utilization of $\text{Ti}_3\text{C}_2\text{T}_x$ and Ti_3CNT_x MXenes for hydrogenation of furfural to furfuryl alcohol. Despite their similar activities ($72 \text{ mmol.g}^{-1}.\text{h}^{-1}$ for Ti_3CNT_x and $88 \text{ mmol.g}^{-1}.\text{h}^{-1}$ for $\text{Ti}_3\text{C}_2\text{T}_x$) and selectivities (49% for Ti_3CNT_x and 52% for $\text{Ti}_3\text{C}_2\text{T}_x$), Ti_3CNT_x was more stable than $\text{Ti}_3\text{C}_2\text{T}_x$, which was justified by the fact that $\text{Ti}_3\text{C}_2\text{T}_x$ was enriched with abundant OH surface terminations, leading to the intercalation reactions between the layers and faster deactivation. In contrast, the N atom in Ti_3CNT_x outstandingly diminished OH terminations, resulting in a decrease in the intercalation reactions.

4.1.5. Selective hydrogenation of butadiene to butene

Selective hydrogenation is crucial in industrial processes, albeit challenging due to the potential hydrogenation of various functional groups [395,404]. Yan *et al.* [405] have demonstrated the capability of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene to serve as a support for atomically dispersed Pt/Pd nanoparticles, owing to its ability to provide vacancies for single atoms. $\text{Ti}_3\text{C}_2\text{T}_x/\text{Pt-Pd}$ catalysts have proven effective in the selective hydrogenation of butadiene, a process important for generating butenes, key monomers in the polymer industry. This study investigates the effect of different etching methods on the catalytic hydrogenation of butadiene. It was found that the LiF-HCl method is preferable to the HF method due

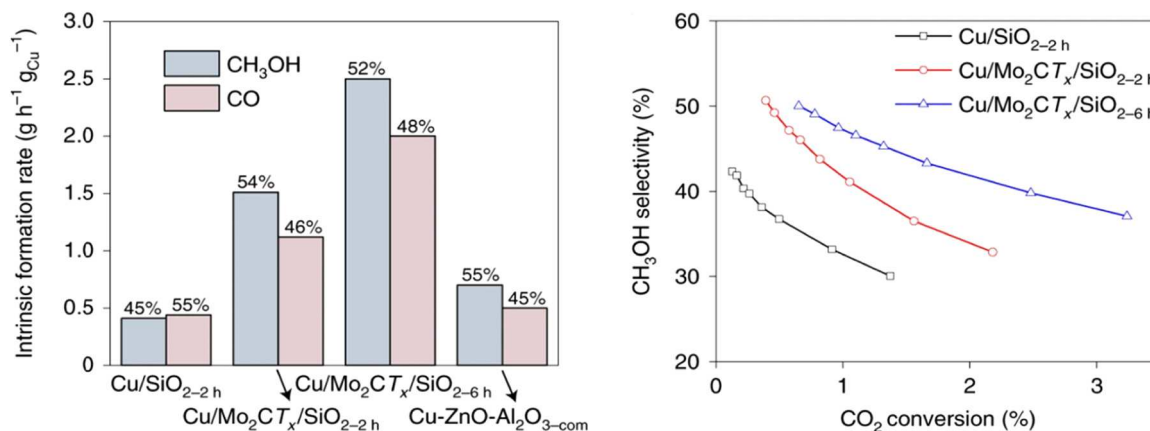


Fig. 21. Comparison of Cu/SiO_2 containing Mo_2CT_x MXene and pristine Cu/SiO_2 regarding (a) performance in intrinsic methanol formation rate and (b) methanol selectivity. Reprinted with permission from [392].

Table 10

Catalytic performance of MXene and MAX-based catalysts in hydrogenation reactions of nitro derivatives.

Catalyst	Reactant	Conversion (%)	Reaction time	Ref.
Pd/Ti ₃ C ₂ T _x Cgraphene hydrogels	4-Nitroaniline	91	1 min	[399]
	4- Chloronitrobenzene	~15	1 min	
	4-Bromonitrobenzene	~48	1 min	
	4-Nitrotoluene	~63	1 min	
	4-Nitrophenol	~70	1 min	
0.0005 wt% Pd/Ti ₃ SiC ₂ DP Pt/Ti ₃ C ₂ T _x -D ^a -AB ^b	4-Nitrostyrene	100	-	[400]
	4- Chloronitrobenzene	100	1 h	
	2- Chloronitrobenzene	100	1.5 h	[401]
	3- Chloronitrobenzene	100	2 h	
	4-Nitrotoluene	100	-	
	2-Nitrotoluene	100	-	
	2-Methoxy-1-nitrobenzene	100	3 h	
	4-Nitrophenol	100	1.5 h	
	2-Fluoronitrobenzene	100	-	
	Nitrobenzene	100	1 h	
	4- Chloronitrobenzene	40.4	-	
Pt/Ti ₃ C ₂ T _x -D ^a -SB ^c				

^a D=decorated on^b AB= ammonia borane (reducing agent)^c SB= sodium borohydride

to its safer nature and efficient delamination, resulting in enhanced metal dispersion and facile unstacking with solid substrates. These two factors contribute significantly to notable hydrogenation performances.

4.1.6. Fischer–Tropsch process

The Fischer–Tropsch (F-T) process has long been used to produce chemicals and fuels through the hydrogenation of CO [406]. The F-T

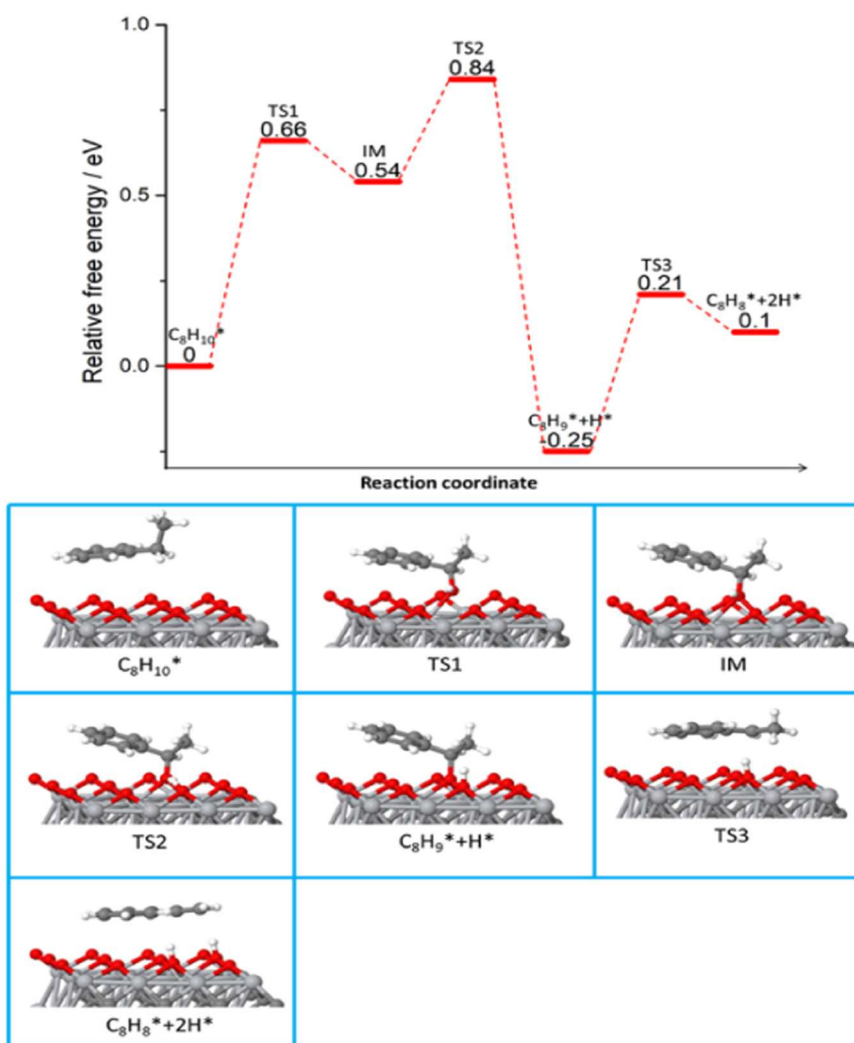
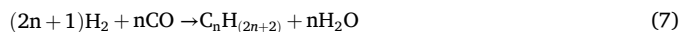


Fig. 22. Reaction pathway of EB dehydrogenation on Ti₃C₂T_x. Light gray, dark gray, red, and white colors denote Ti, C, O, and H atoms, respectively. Reprinted with permission from [409].

reaction is [407]:



Kountoupi et al. [408] found that Mo_2CT_x -derived catalysts can be employed for this reaction. Their results indicated that the selectivity of the F-T reaction is contingent upon the coverage of surface oxygen and carbide content. In this regard, Mo_2CT_x pretreated at 500 °C (Mo_2CT_{x-500}) in undiluted H_2 is more active than Mo_2CT_x pretreated at 400 °C (Mo_2CT_{x-400}), which is ascribed to the oxygen content. Moreover, the study revealed that these two catalysts differ in selectivity at ca. 90% CO conversion. Specifically, Mo_2CT_{x-400} is more selective towards C_{5+} alkanes and Mo_2CT_{x-500} to methane (55 and 61%, respectively). This discrepancy is related to the differences in the structure (and the active sites) and, in particular, the substoichiometric carbidic carbon content in Mo_2CT_{x-400} . Also, DFT calculations indicated substantial differences between the reaction barriers and the stability of intermediates on 2D- Mo_2C and those achieved for 3D- Mo_2C , with H-assisted CO dissociation pathway (leading to HCO^* and COH^* intermediates) being dominant in the latter and carbidic chain growth mechanism in the former.

4.2. Dehydrogenation reactions

The production of alkene monomers from hydrocarbons is of great importance, specifically in the polymer industry. However, these reactions require high temperatures (~600 °C) and high levels of steam, and the lack of stability of their catalysts due to coke formation is a major issue. MXenes have been found to serve as catalysts or supports for direct dehydrogenation (DDH) of oxidative dehydrogenation (ODH) reactions [55]. One of the DDH applications of MXenes is the synthesis of styrene, a pivotal monomeric compound, from ethylbenzene (EB). Specifically, Diao et al. [409] conducted research associated with $Ti_3C_2T_x$ MXene-catalyzed EB dehydrogenation. They prepared a $Ti_3C_2T_x$ MXene terminated with O groups through an etching method, the dehydrogenation pathway of which is depicted in Fig. 22. The as-synthesized $Ti_3C_2T_x$ MXene led to an EB conversion rate of 92 $\mu mol\ m^{-2}\ h^{-1}$, whereas those of graphene, nanodiamond, and TiC-derived carbon (TiC-CDC) were 12, 7, and 0.8 $\mu mol\ m^{-2}\ h^{-1}$, respectively. Furthermore, the styrene selectivity of the MXene-based catalyst was as high as 97.5%, which was comparable to other mentioned carbon catalysts (Fig. 23A). A long-run stability test was also conducted to confirm the long-term activity of the $Ti_3C_2T_x$ catalyst. Interestingly, the outcomes indicated that EB conversion rate (%) remained at 21% for nearly 40 h, demonstrating no deactivation and coke formation (Fig. 23B).

4.3. Oxidation of CH_4 and CO

Methane (CH_4) is considered one of the most critical fuel gases in a myriad of industrial applications. Nonetheless, CH_4 can be converted into methanol in a stepped manner because it is challenging to stop the product selectively after the first C-H activation without deactivating the catalyst [410]. Consequently, potential catalysts are necessary for directly converting methane to methanol. In this regard, MXenes have proven efficient as applicable supports for SACs. For instance, Sun and coworkers [411] modeled Mo_2CO_2 -supported Pd monomer and dimer (Pd_2) and compared their abilities in methane conversion to methanol. The electronic and geometrical configurations results showed that Mo_2CO_2 can support anchor Pd dimer. Additionally, calculations illustrated the suitable adsorption of CH_4 and O_2 onto the Pd_2/Mo_2CO_2 surface due to its multiple active sites.

The seemingly facile CO oxidation reaction:



is of great significance in controlling pollution and the separation of CO from H_2 fuel [412]. In this regard, heterogeneous catalysts like Pd

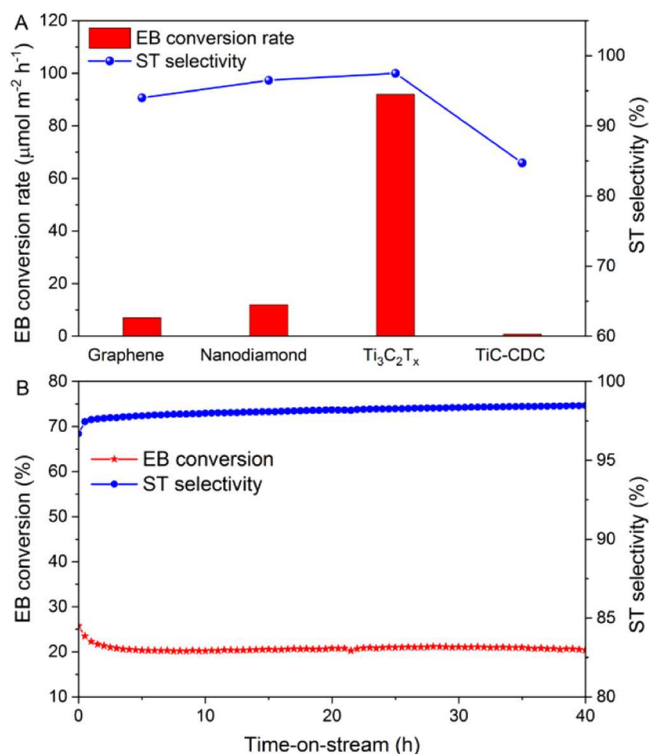


Fig. 23. (A) Comparison of EB conversion rate and styrene (ST) selectivity between $Ti_3C_2T_x$ MXene and three carbon-based catalysts and (B) the stability test of $Ti_3C_2T_x$ MXene on dehydrogenation of EB. Reprinted with permission from [409].

and Cu can be potentially harnessed to accelerate this reaction [413]. From a theoretical standpoint, MXenes can be potentially utilized as heterogeneous catalysts for CO oxidation, for which three possible reaction pathways are plausible: the Langmuir–Hinshelwood (LH), the traditional Eley–Rideal (ER), and the trimolecular Eley–Rideal (TER) mechanisms [414]. Among these pathways, the LH mechanism is the most feasible, although the occurrence of the appropriate pathway generally depends on the level of the rate-determining energy barrier [415]. Schematics of CO oxidation through LH and ER mechanisms on Ag(111) surfaces are depicted in Fig. 24.

Computational methods such as ab initio molecular dynamics have shown dynamic and thermal stabilities of Mo_2CS_2 monolayer [417]. Peng and coworkers [418] modeled a Ti_2CN_2 MXene-supported Zn catalyst and investigated its performance in CO oxidation. DFT calculations revealed that ER is the most probable mechanism for CO oxidation with a tiny barrier (only 0.06 eV), allowing the reaction to progress at low temperatures. In the ER mechanism, CO reacts with already pre-adsorbed O_2 and proceeds as follows: $CO + O_2^* \rightarrow CO_2 + O^*$ and $CO + O^* \rightarrow CO_2$. Based on the density of states, Bader charge, and other electronic structure analysis, the high catalytic activity of Ti_2CN_2/Zn was attributed to the structure of single atom Zn, which instigates the activation of O–O bond. In a comparative study, Cai et al. [419] computationally assessed the catalytic activity of Sc and Ti-anchored Zr_2CO_2 (MXene) in CO oxidation in incomplete combustion gas (O_2 , CO, N_2 , and CO_2). Due to its high barrier energy, the Ti/ Zr_2CO_2 catalyst was more efficacious than Sc/ Zr_2CO_2 . According to DFT studies, they concluded that CO oxidation can progress by both LH and ER mechanisms. In addition, after O_2 was adsorbed, it remarkably remained to replace other pre-adsorbed gases, showcasing that both catalysts could resist the disturbance of the major gases so that a CO oxidation reaction was possible. A systematic DFT investigation of the catalytic activity of Ti_2CO_2 MXene-supported single atom catalysts M_1/Ti_2CO_2 ($M = Fe, Co, Ni, Cu, Ru, Rh, Pd, Ag, Os, Ir, Pt, Au$) by Zhu et al. [420]

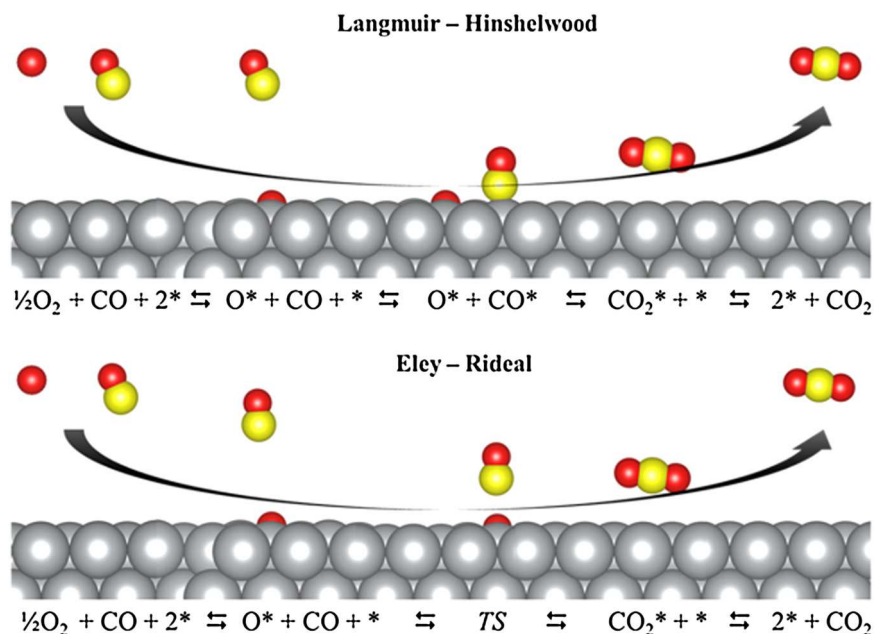


Fig. 24. Different mechanisms of CO oxidation on Ag(111) surface: (a) Langmuir–Hinshelwood mechanism of CO and O₂ co-adsorption and (b) Eley–Rideal mechanism of just O₂ adsorption. TS denotes the transition state. Reprinted with permission from [416].

revealed that the Fe-containing catalyst, with a distinct low-energy barrier (0.2 eV), has the most favorable catalytic performance.

4.4. Dry reforming of methane

DRM reaction is the reaction of CH₄ and CO₂ that generates CO and H₂, which in turn allows to alleviate CH₄ and CO₂ concentrations as greenhouse gases [421]:



Thakur *et al.* [422] investigated the catalytic performance of V₂O₃-V₈C₇. In this research, an m-V₂CT_x MXene was utilized as a precursor to the 3D V₂O₃-V₈C₇ phases since, like other multilayered thin MXenes, m-V₂CT_x MXene is unstable at high temperatures [423]. Therefore, the m-V₂CT_x phase was initially pre-treated in N₂ at 800 °C, decomposing m-V₂CT_x to V₂O₃-V₈C₇, which was then utilized as a catalyst. The study showed that the DRM activity of V₂O₃-V₈C₇ (converting 78% CH₄ and 82% CO₂) is comparable to that of the nickel catalyst supported on zeolite Socony Mobil-5 (ZSM-5). Furthermore, it was discovered that stability in high temperatures, anti-oxidation characteristics under mild oxidative situations, and the ability to participate in oxidation-carburization cycles are pivotal properties in the dry reforming of methane and other hydrocarbons. Although a MXene was not used as a direct catalyst in DRM, it was employed as a precursor for the leading catalysts. In another research, Kurllov *et al.* [424] dispersed Mo₂CO₂ MXene on silica, showing high catalytic activity and stability in the dry reforming of CH₄. DFT calculations verified CH₄ activation on oxygen sites to form *OCH₃ and *OH. It is worth mentioning that the idea of depositing Mo₂CO₂ on the surface of silica was to hinder the thermal transformation into bulk Mo₂C, augmenting the accessibility of Mo sites and hampering catalyst deactivation. The results indicated that the consumption rate of CH₄ using Mo₂CO₂/SiO₂ was ~10–200 times higher compared to the bulk counterpart. Huang *et al.* [425] also conducted research on a sintered V₂C-V₂O₃ (m-V₂C-V₂O₃)-supported Ni as a potential heterogeneous catalyst for DRM. The synthesized catalyst showed high stability and activity in a 90-hour cycle of utilization. Ni/ m-V₂C-V₂O₃ led to optimal CH₄ and CO₂ conversion rates of 94% and 89%, respectively.

5. Conclusion and perspectives

In conclusion, the versatile and remarkable properties exhibited by MXenes underscore their potential across a spectrum of applications, ranging from electromagnetic interference shielding to flexible optoelectronics, sensors, thermal heaters, and nanocomposites. The recent surge in exploring MXenes as heterogeneous catalysts for diverse reactions reflects a strategic response to the challenges posed by the scarcity and elevated costs of noble metals inherent in traditional catalysts. MXenes, with their abundance and cost-effectiveness, present a viable alternative that has garnered significant research attention.

This review has provided a summary of recent advances in leveraging MXenes for catalytic activities, emphasizing their efficacy in reactions such as hydrogen evolution, oxygen evolution, oxygen reduction, nitrogen reduction, carbon dioxide reduction, alcohol oxidation, hydrogenation, dehydrogenation, methanol conversion, dry reforming of methane, and Fischer-Tropsch synthesis. The exploration of these catalytic applications has opened new avenues for MXenes, expanding their role beyond traditional material applications.

Despite these promising developments, challenges persist, and further research is required to address issues such as scalability, stability, and optimization of catalytic performance. As the field continues to evolve, this review serves as a valuable resource for researchers, offering insights into the current state of MXene-based catalysis, highlighting challenges, and outlining prospective directions for future investigations. The inexhaustible potential of MXenes in catalysis positions them as pivotal contributors to the ongoing evolution of advanced materials and catalytic technologies.

Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Masoud Soroush reports financial support was provided by National Science Foundation. Masoud Soroush reports a relationship with National Science Foundation that includes: funding grants. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

M.S. would like to acknowledge financial support from the U.S. National Science Foundation under Grant No. CMMI-2134607. Any opinions, findings, and conclusions or recommendations expressed in this material are those of the authors and do not necessarily reflect the views of the National Science Foundation. The authors would also like to thank the anonymous reviewers for their careful constructive comments.

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