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Recent advances of MXenes as electrocatalysts for hydrogen evolution reaction

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MXenes, an emerging two-dimensional (2D) transition metal carbides, nitrides and carbonitrides, have exhibited great potential as electrocatalysts for hydrogen evolution reaction (HER) due to the excellent characters, including excellent structural and chemical stability, superior electrical conductivity, and large active surface area. In this comprehensive study, firstly, the preparation advances of MXenes are systematically summarized. Then, the representative applications of MXenes-based HER electrocatalysts are introduced, from experimental and theoretical aspects. Thirdly, the strategies for improving HER catalytic activity of MXenes are demonstrated, such as optimizing active sites by termination modification and metal-atom doping, increasing active sites by fabricating various nanostructures. Finally, the existing challenges and new opportunities for MXenes-based electrocatalysts are also elucidated. This paper provides reference for the future development of new and efficient MXenes-based electrocatalysts for hydrogen production through water-splitting technology.

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INTRODUCTION

With the growing problems of energy shortage and environmental pollution in the world, hydrogen has received extensive attention. Hydrogen has several advantages including high energy density, zero pollution emission, no greenhouse gas emission, recycling and so on. It can be well compatible with the green energy storage and conversion fields, with the merits of safety, efficiency, low-cost, sustainability, and environmental friendliness. Hydrogen can be prepared via various approaches, including burning of fossil fuels or biomass feed stock, fermentation of marsh gas or organic waste. Of which, the water-splitting based HER has been an economic and environmentally-friendly approach¹.

The electrocatalyst is significant in HER for obtaining hydrogen, in which the precious metal-based electrocatalysts (such as Pt, Ru) exhibit good efficiency and stability. However, the ever-increasing demand for precious metal-based electrocatalysts has been hampered by limited resources and rising cost. Therefore, further development of high-efficient non-precious metal (NPM) based HER electrocatalysts for preparing hydrogen has been a pressing challenge^{2–5}. Till now, considerable achievements have been made and following electrode materials have been developed: phosphides⁶, carbides⁷, sulfides⁸, nitrides⁹, oxides¹⁰, and even metal-free nanocarbons. There are still two main problems: one is the poor electrical conductivity, leading to the thickening of the active coating and sharp decline of activity. The other one is the insufficient electrochemical reaction stability of these NPM based materials in aqueous electrolytes. With the advances of materials, MXenes, known as the graphene-like two-dimensional (2D) transition metal carbides, carbonitrides, or nitrides, show the potential to overcome above-mentioned problems. Attributed to the high carrier mobility and intrinsic layered structure, MXenes have been regarded as a class of promising HER electrocatalysts.

Since $Ti_3C_2T_x$ were discovered by Gogotsi's group in 2011, MXenes have received increasing attention resulted from the excellent characters, including excellent structural and chemical stability, superior electrical conductivity, and large active surface area^{11–13}. So far, more than 30 MXene compositions have been synthesized, and more than 100 kinds have been studied through computational methods. In addition, MXenes has also evolved from the initial type containing only one or two transition metals to the current four transition metal high-entropy 2D carbide MXenes ($TiVNbMoC_3$, $TiVCrMoC_3$), and its variety has been greatly increased¹⁴. MXenes can be demonstrated with a general chemical formula: $M_{n+1}X_nT_x$, where M is early transition metal atoms, such as Ti, Zr, Nb, and V; X is carbon or nitrogen; n presents 1, 2, 3 or 4; T_x is the surface termination group, such as $-F$, $-OH$, or $-Se$, further, the M layers cover the X layers in $[MX]_nM$ arrangement¹⁵. MXenes are generally produced from ternary metal carbides or nitride precursors MAX phase. MAX phase can be demonstrated with a general chemical formula: $M_{n+1}AX_n$, where A is generally group 13–14 elements (i.e., Al, In, Si, Pb) and late transition metals (e.g., Zn, Cu, Ni, and Co); M layers are terminated with hydrophilic groups ($-O$, $-OH$, or $-F$)¹¹. During the preparation, the $M_{n+1}AX_n$ precursors are treated with concentrated hydrofluoric acid (HF), or a mixed solution of lithium fluoride and hydrochloric acid (HCl). The A layer can be selectively extracted without breaking the M–X bonds. Few-layered MXenes are gained from the exfoliated MXenes, by sonicating in organic solvent such as dimethyl sulfoxide (DMSO). Additionally, few-layered MXenes possess multilayer structure (less than 1 nm in thickness) and millimeter-scale lateral dimension¹⁶.

With extensive investigation, MXenes are evidenced as potential alternatives for hydrogen storage¹⁷, batteries^{18,19}, electromagnetic interference shielding^{20,21}, catalysis^{22–24}, sensors^{25–30}, supercapacitors^{31–34}, and so on^{35–37}. MXenes have shown great potential as HER electrocatalysts for several special advantages, such as

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excellent metallic conductivity (up to $10,000 \text{ S cm}^{-1}$), large surface area, adjustable structure, and good hydrophilicity. Several advances have been made in designs and applications of MXenes-based materials, including MXenes nanosheets and composites. Here in this review, we firstly introduce the preparation of MXenes, then lay emphasis on recent progress on MXenes-based HER electrocatalysts, finally we also focus on the strategies for optimizing the properties of these electrocatalysts.

SYNTHESIS STRATEGIES OF MXENES

In recent years, extensive efforts have been invested to develop diverse routes for preparing MXenes in cost and energy-economic strategies. The clean production and green chemistry should be ever-increasingly considered in producing MAX phase materials. So far, MXenes have been generally prepared from MAX phase with fluoride etching, alkali treatment, electrochemical etching, and water-free etching, which will be discussed in this section (Fig. 1). The corresponding comparisons of different etching methods for the synthesis of MXenes are listed in Table 1.

Fig. 1 Synthesis strategies of MXenes. Schematic diagram summarizing different synthesis techniques of MXenes.

Fluoride etching

There are two general ways for performing fluoride etching. One is direct etching with concentrated HF. The MAX phase is etched at room temperature under constant agitation, then MXenes with multilayer structures are exfoliated by sonicating in methanol and isopropyl alcohol. The other is reaction-generated HF in situ³⁸ from HCl and fluorides, including LiF³⁹, NaF⁴⁰, KF⁴¹, CsF³⁹, CaF³⁹, FeF₃⁴¹, and tetra-n-butyl ammonium (Fig. 2a)³⁹. SEM analysis shows Ti₃AlC₂ (Fig. 2b) has a layered structure, resemble to the 'accordion'. Restacked multi-layers with obvious sheet gaps could be observed in the particles after etching MAX (Fig. 2c). SEM, TEM and high-resolution TEM image of as-prepared monolayered Ti₃C₂T_x (MXene) nanosheets revealed electron-transparent foils with thin, smooth surfaces and diameters ranging from 100 nm to several micrometers (Fig. 2d–f).

The synthesis of MXenes has been reported by Naguib et al.¹², referring to the chemical reaction between MAX phase and fluorine-rich aqueous environment. The Al atoms were removed (reaction 1), and the MXenes were terminated with –OH and –F (reaction 2 and 3, respectively). The oxygen termination was also observed in MXenes. In other words, the Ti–Al bond was replaced by Ti–F, Ti–OH, or Ti–O. Several MXenes can be successfully obtained with this method, such as TiC₂T_x⁴², Ti₃CNT_x⁴³, TiNbCT_x⁴⁴, Ti₃C₂T_x⁴⁵, Mo₂Ti₂C₃T_x⁴⁶, Nb₂CT_x⁴⁷, Zr₃C₂T_x⁴⁸, (Nb_{0.8}Ti_{0.2})₄C₃T_x⁴⁹, and (Nb_{0.8}Zr_{0.2})₄C₃T_x⁴⁹.

Etching with HF or other fluorinated solutions has been successfully applied in the development of MXenes, which has become a standard preparation method for MXenes. However, this method shows several problems. First, the Al atoms in MAX-phase precursors show high reactivity with F[–] and it limited the synthesis of various MXenes due to fluoride-based aqueous solutions mainly effective for Al-containing MAX-phase precursors. Second, the involvement of HF leads to safety and environmental problems. Third, the resulted inert F-terminal reduces material performance, thus hindering the further applications of MXenes. To sum up, it is significant to develop innovative HF-free etching strategies.

Alkali etching

Theoretically, alkali is ideal for etching Ti₃AlC₂ because of the good reactivity with amphoteric Al. The difficulty in obtaining MXenes by alkali etching is in reaction kinetics, and some oxides/hydroxides will be formed on the surface of Ti₃AlC₂ during alkali treatment^{50–53}. Li et al.⁵³ reported that KOH could be applied as an etching agent for MXenes preparation, and nanoscale tablets of

Table 1. The comparisons of etching methods for the synthesis of MXenes.

Synthetic method	Disadvantage	Advantage	Ref.
Fluoride etching	(1) High toxicity of HF (2) Lower HER activity	(1) Accordion-like structure (2) Small flake size	38–49
Alkali etching	(1) Formation of some oxides/hydroxides may further hinder the required Al extraction.	(1) Avoid the use of HF (2) Remove the amphoteric or acidic atoms from original MAX phase.	50–54
Electrochemical etching	(1) Low yield	(1) Avoid the use of HF (2) Extend the range of etching techniques and potential compositions of MXenes. (3) Fabricate MXenes difficult to prepare	55–57
Water-free etching	(1) High temperature (2) Low hydrophilicity	(1) Expand the selection range of MXene precursor MAX phase (2) Provide a green and viable route to prepare MXenes	58–61

Fig. 2 The synthesis of MXenes from MAX phase by fluoride etching. **a** Schematic diagram of MAX phase etching and MXenes formation. **b** SEM image of MAX phase before HF etching. **c** SEM image of multilayer $\text{Ti}_3\text{C}_2\text{T}_x$ after HF etching⁴⁴. Copyright 2012, American Chemical Society. **d–f** SEM, TEM and high-resolution TEM images of monolayer $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheet⁴⁵. Copyright 2019, American Chemical Society.

Fig. 3 The synthesis of MXenes from MAX phase by NaOH etching. **a–d** The NaOH etching of Ti_3AlC_2 under different temperatures and NaOH concentrations. **e** The $\text{Ti}_3\text{C}_2\text{T}_x$ products under different hydrothermal treatment conditions. **f** SEM, **g** TEM, and **h** HAADF-STEM characterizations of the $\text{Ti}_3\text{C}_2\text{T}_x$ flakes. The bright spots in **h** indicate Ti atoms⁵⁴. Copyright 2018, WILEY-VCH.

Fig. 4 The synthesis of MXenes from MAX phase by electrochemical etching. **a** The configuration of electrochemical cell. **b** The potential mechanism for electrochemical etching of Ti_2AlC with HCl as electrolyte⁵⁵. Copyright 2017, Royal Society of Chemistry. **c** The mechanism of pseudocapacitive contribution of various Ti_2CT_x ⁵⁷. Copyright 2019, American Chemical Society. **d** X-ray diffraction patterns of Ti_3AlC_2 , $\text{Ti}_3\text{C}_2\text{T}_x$, and $\text{Ti}_3\text{C}_2\text{T}_x$ films. **e** Electron localization function plots for pristine and etched Ti_3AlC_2 . **f–g** SEM images and **h** TEM image of the delaminated $\text{Ti}_3\text{C}_2\text{T}_x$. Inset in **h** shows the selected area electron diffraction (SAED) result⁵⁶. Copyright 2018, WILEY-VCH.

single-layer $\text{Ti}_3\text{C}_2(\text{OH})_2$ were successfully prepared. However, with alkali exposure, the formation of Al oxide/hydroxide layers, such as $\text{Al}(\text{OH})_3$ and $\text{AlO}(\text{OH})$, may further hinder the required Al extraction. In xie' s work⁵⁰, only the aluminum atoms were removed from the outer surface of Ti_3AlC_2 . Besides, Zou et al.⁵² reported that some Na/K-Ti-O compounds rather than MXene were produced while the alkali treatment removed part of the aluminum. Therefore, these oxidation layers must be removed.

NaOH assisted hydrothermal etching of Ti_3AlC_2 was reported to prepare $\text{Ti}_3\text{C}_2\text{T}_x$ ($\text{T} = \text{OH}, \text{O}$) (Fig. 3a–e)⁵⁴. This hydrothermal treatment was carried out in an argon atmosphere to minimize the oxidation of the sample. The multilayer $\text{Ti}_3\text{C}_2\text{T}_x$ could be obtained by selective removal of Al in Ti_3AlC_2 with NaOH solution at 270 °C. The purity of product with OH and O terminal groups was 92 wt%, without observable F terminal group. The SEM image of $\text{Ti}_3\text{C}_2\text{T}_x$ (270 °C, 27.5 M NaOH) shows a compact layered structure (Fig. 3f). The morphologies of these $\text{Ti}_3\text{C}_2\text{T}_x$ (MXene) nanosheets were analyzed by TEM and HAADF-STEM (Fig. 3g–h). It indicates that $\text{Ti}_3\text{C}_2\text{T}_x$ sheets have a nonuniform interlayer spacing of ~1.2 nm, which is larger than the pristine Ti_3AlC_2 (0.93 nm). The mass capacitance and volume capacitance of the $\text{Ti}_3\text{C}_2\text{T}_x$ thin film electrode was up to 314 F g^{-1} and 511 F cm^{-3} . Compared with the multilayer $\text{Ti}_3\text{C}_2\text{T}_x$ prepared by HF, the mass capacitance was increased by 214%. This alkali etching method succeeds to

remove the amphoteric or acidic atoms from original MAX phase. It provides a HF-free strategy for developing innovative MXenes.

Electrochemical etching

Chemical etching is based on the reactivity difference between M-Al and M-C bond. However, electrochemical etching refers to the direct transfer of charge. Sun et al.⁵⁵ demonstrated the successful electrochemical extraction of Al on porous Ti_2AlC electrode in diluted HCl solution. A layer of Ti_2CT_x MXenes can be obtained on Ti_2AlC (Fig. 4a). Compared to chemical etching using HF or LiF/HCl , the electrochemical etching method did not involve any F ion, thus obtaining MXenes with only -Cl, -O and -OH groups. However, the problems in electrochemical etching may be the over-etching of MAX phase into carbines-derived carbon (CDC). A core-shell model was proposed to interpret how the Ti_2AlC was electrochemically etched to Ti_2CT_x and CDC (Fig. 4b). It indicated that etching parameters should be carefully balanced to generate MXenes while avoiding overloading. The electrochemical etching has extended the range of etching techniques and potential compositions of MXenes.

Yang et al.⁵⁶ demonstrated an effective strategy to fabricate $\text{Ti}_3\text{C}_2\text{T}_x$ ($\text{T} = \text{O}, \text{OH}$) MXenes by electrochemical corrosion (Fig. 4d–e). By adjusting the composition of the electrolytes, Al atoms

can be selectively removed, and then replaced with hydroxyl groups. Thus, single-layer or double-layer $\text{Ti}_3\text{C}_2\text{X}_n$ nanosheets can be formed, with large average size and a yield higher than 90%. SEM images (Fig. 4f) reveal that $\text{Ti}_3\text{C}_2\text{X}_n$ sheets have irregular edges and mostly dispersed size distribution generally ranging from 1 to 5 μm , due to an exfoliation-fragmentation mechanism. Under mild etching conditions, the diameters of some larger slices can reach 18.6 μm (Fig. 4g). TEM image (Fig. 4h) displays a typical $\text{Ti}_3\text{C}_2\text{X}_n$ sheet with well-defined and clean edges. The results were similar or even superior to chemical etching techniques. The obtained $\text{Ti}_3\text{C}_2\text{X}_n$ thin film was applied to assemble solid supercapacitors for energy storage. The area capacitance can be up to 220 mF cm^{-2} . In addition, neither dangerous fluorinated agent was required, nor tough etching conditions. It is suitable for the preparation of innovative MXenes.

A thermal-assisted electrochemical etching has been reported⁵⁷. MXenes were prepared under HF-free conditions, including Ti_2CT_x , Cr_2CT_x , and V_2CT_x . A three-dimensional (3D) composite electrode was applied. In the presence of diluted HCl as etchant, gentle heating sped up the etching reaction of MAX phase, thus greatly improving the etching efficiency of MXenes. Since Ti-based MXenes have been widely prepared, Ti_2CT_x was selected as a typical example in this study. Ti_2CT_x was prepared by electrochemical etching following a two-stage strategy. In the stage 1, Al atoms were firstly removed from layered structure under the effects of applied voltage, since the Ti-Al bond was easier to be broken compared to the Ti-C bond. The MXenes can

be obtained. In the stage 2, Al and Ti atoms would be completely removed, leaving only monolayer carbon atoms. By controlling the etching time, temperature, and electrodes, the MXenes with different morphologies can be obtained. With this method, another two MXenes (V_2C and Cr_2C) can be successfully obtained, which were generally considered difficult to prepare. In previous reports, V_2C required HF corrosion for more than two days, with a HF concentration of up to 50%. The Cr_2C had not been successfully prepared. The thermal-assisted electrochemical etching has not only proposed a universal strategy for the synthesis of MXenes, but also fabricated MXenes difficult to prepare. It opens a window for preparing MXenes in a rapid, facile and safe way.

Water-free etching

At present, the methods of non-aqueous etching include molten salt etching (Lewis acid etching) and iodine assisted etching. The reaction of MAX phase in molten salt (Lewis acid) was similar to that of in HF, such as the reaction of Ti_3AlC_2 in molten ZnCl_2 ⁵⁸. The Ti_3ZnCl_2 MAX phase was obtained by substitution reaction, and then it was transformed into $\text{Ti}_3\text{C}_2\text{Cl}_2$ MXenes by increasing the ratio of MAX: ZnCl_2 . After optimizing the reaction, a class of $\text{M}_{n+1}\text{ZnX}_n$ phases were prepared through substitution reaction, thus obtaining corresponding MXenes ($\text{M}_{n+1}\text{X}_n\text{Cl}_2$) with Cl group on the surface.

Following the report of MXenes synthesis by molten Lewis acid in 2019, Huang et al.⁵⁹ carried out in-depth and systematic

Fig. 5 The synthesis of MXenes from MAX phase by Lewis acid etching. **a** Surface etching and delamination of MXenes in molten salts. **b** TEM image of $\text{Ti}_3\text{C}_2\text{Cl}_2$ MXenes flakes. **c** Negative zeta potential of the delaminated MXenes in N-methylformamide (NMF). **d** The correlation of the in-plane lattice constant (a) and surface group (T_n) for Ti_2CT_n and $\text{Ti}_3\text{C}_2\text{T}_n$ MXenes. **e** Surface groups and the corresponding biaxial straining of $\text{Ti}_3\text{C}_2\text{T}_n$ MXenes lattice. **f, g** Electronic transport and superconductivity in Nb_2CT_n MXenes⁶⁰. Copyright 2020, American Association for the Advancement of Science.

Fig. 6 The synthesis of MXenes from MAX phase by non-aqueous iodine-assisted etching. **a, b** The iodine-assisted etching and delamination of Ti_3AlC_2 towards 2D MXene sheets. **c** XRD patterns of MAX phase, I_2 -etched MAX, and 2D IE-MXene flakes. **d** SEM image of MAX phase. **e** SEM image of I_2 -etched MAX. **f** SEM image of 2D IE-MXene flakes⁶¹. Copyright 2021, John Wiley and Sons Ltd.

research, then proposed the strategy of preparing MXenes with general molten salt. The redox potential of Lewis acid cations was so high as to oxidize the A-layer atoms in the MAX phase. Under the guidance of this redox potential-based rule, a variety of molten salts (CdCl_2 , FeCl_2 , CoCl_2 , CuCl_2 , AgCl , NiCl_2) were further applied to etching different MAX phases (Ti_2AlC , Ti_3AlC_2 , Ti_3AlCN , Nb_2AlC , Ta_2AlC , Ti_2ZnC , Ti_3ZnC_2) to prepare the corresponding MXenes. These results suggested that in the traditional MAX phase, A element can be replaced with the late transition metal halide. It has greatly expanded the range of MAX phase as precursors of MXenes. As a HF-free method, Lewis acid etching provides a green and feasible way for preparing MXenes.

The range of Lewis acid etching can be further expanded. In the study of Dmitri V. Talapin⁶⁰, MAX phase was first treated with molten CdCl_2 to prepare $\text{Ti}_3\text{C}_2\text{Cl}_2$, Ti_2CCl_2 , and Nb_2CCl_2 with Cl-terminated group. Then, the Br-terminated MXenes were also prepared using CdBr_2 molten salts. Concerning the surface groups, the bond energy of the Ti-Cl bond (405 kJ mol^{-1}) or the Ti-Br bond (373 kJ mol^{-1}) in these MXenes was much weaker than that of the Ti-F bond (569 kJ mol^{-1}) or the Ti-O bond (666 kJ mol^{-1}) in the classical MXenes. The termination of transformation chemistry was further explored. $\text{Ti}_3\text{C}_2\text{Br}_2$ was dispersed into molten CsBr/KBr/LiBr , then Li_2Te or Li_2S was added to obtain $\text{Ti}_3\text{C}_2\text{Te}$ or $\text{Ti}_3\text{C}_2\text{S}$, respectively. Similarly, they also converted $\text{Ti}_3\text{C}_2\text{Cl}_2$ to $\text{Ti}_3\text{C}_2\text{Te}$, $\text{Ti}_3\text{C}_2\text{S}$, and $\text{Ti}_3\text{C}_2(\text{NH})$. Interestingly, LiH was able to reduce $\text{Ti}_3\text{C}_2\text{Br}_2$ and Ti_2CBr_2 to $\text{Ti}_3\text{C}_2\Box$ and $\text{Ti}_2\text{C}\Box$ (where $\Box$ indicated defect) at 300°C . Above samples were further treated with n-butyl

lithium (n-BuLi) for obtaining the product with Li intercalation layer, which could be further dispersed in polar organic solvents to form monolayered product (Fig. 5a). TEM image of $\text{Ti}_3\text{C}_2\text{Cl}_2$ monolayered displays crystallinity and hexagonal symmetry of the individual flake (Fig. 5b–c) and negative zeta potential (-29.3 mV). Termination transformation was accompanied by the dramatic change of lattice structure (Fig. 5d–e), indicating that surface modification made a great impact on all aspects of MXenes performance. The electron transport operation of the Nb_2C MXenes was examined (Fig. 5f–g). The superconducting transition temperature of Nb_2CCl_2 was about 6 K, while the bulk phase of Nb_2AlC was not superconductive.

Recently, Shi et al.⁶¹ reported a non-aqueous iodine (I_2) assisted etching route for the synthesis of 2D MXene with oxygen-rich terminal groups. The $\text{Ti}_3\text{C}_2\text{I}_x$ was firstly prepared through iodine etching in anhydrous acetonitrile at 100°C , followed by the stratification in HCl solution to further transformed $\text{Ti}_3\text{C}_2\text{I}_x$ into $\text{Ti}_3\text{C}_2\text{T}_x$ flakes with moderate sizes (ca. $1.8 \mu\text{m}$), over 71% of which were thinner than 5 nm (Fig. 6a, b). In addition, the obtained $\text{Ti}_3\text{C}_2\text{T}_x$ flakes showed an excellent ambient stability in dispersions for at least 2 weeks. The mechanism of the synthetic process was proposed as below:

Table 2. Summary of HER activities of MXene-based electrocatalysts.

Catalyst	Electrolyte	Overpotential at 10 mA·cm ⁻²	Tafel slope (mV·dec ⁻¹)	Ref.
Ti ₃ C ₂ O _x	0.5 M H ₂ SO ₄	190	60.7	75
Ti ₃ C ₂ (OH) _x	0.5 M H ₂ SO ₄	217	88.5	75
Ti ₃ C ₂ T _x -450	0.5 M H ₂ SO ₄	266	109.8	75
Mo ₂ TiC ₂ T _x -Pt _{SA}	0.5 M H ₂ SO ₄	30	30	88
Mo ₂ CT _x : Co	1 N H ₂ SO ₄	180	/	90
Mo ₂ CT _x	1 N H ₂ SO ₄	230	/	90
Ti ₃ C ₂ T _x nanofibers	0.5 M H ₂ SO ₄	169	97	96
Ti ₃ C ₂ T _x flakes	0.5 M H ₂ SO ₄	385	188	96
Pt/Ti ₃ C ₂ T _x	0.1 M HClO ₄	32.7	32.3	117
NiCo@Nb-Ti ₃ C ₂ T _x	1 M KOH	43.4	116	114
MoS ₂ /Ti ₃ C ₂ T _x @C	0.5 M H ₂ SO ₄	135	46	103
NiSe ₂ /Ti ₃ C ₂ T _x	0.5 M H ₂ SO ₄	200	23.7	105
NiS ₂ /V ₂ CT _x	1 M KOH	179	85	106
MoSe ₂ /Ti ₃ C ₂ T _x	1 M KOH	95	91	107
MoS ₂ /Ti ₃ C ₂ T _x nanoroll	0.5 M H ₂ SO ₄	152	70	101
VS ₂ /V ₂ CT _x	1 M KOH	164	47.6	102
BP QDs/Ti ₃ C ₂ T _x	1 M KOH	190	83	124
FeNi@Mo ₂ TiC ₂ T _x @NF	0.5 M H ₂ SO ₄	165	103.46	121

According to the X-ray diffraction (XRD) patterns (Fig. 6c), the characteristic (104) peak of Ti₃AlC₂ ($2\theta = 39^\circ$) in the I₂-etched MAX disappeared, and the (002) peak ($2\theta = 9.8^\circ$) shifted to a lower angle ($2\theta = 6.1^\circ$), which reflected the expansion of interlayer spacing from 9.3 Å to 14.4 Å, thus indicating the successful Al etching. Due to the subsequent washing and delamination, the (002) peak of the 2D IE-MXene shifted to an even lower angle ($2\theta = 5.2^\circ$), indicating the further expansion of interlayer spacing from 14.4 Å to 17.4 Å. The SEM images (Fig. 6d–f) also clearly revealed the morphological changes.

MXENES-BASED ELECTROCATALYSTS FOR HER

Development of hydrogen energy offers an efficient solution to today's environmental and energy issues^{62,63}. HER is an important strategy for water splitting and hydrogen production. It is critical to develop HER catalysts with superior performance in the proposed hydrogen economy, including good conductivity, stability, selectivity etc. The high-performance electrocatalyst can minimize the overpotential necessary for the HER thus improving efficiency^{64,65}. In theory, density functional theory (DFT) calculations can be used to determine the Gibbs free energy of hydrogen adsorption (ΔG_H), which has been proved to be a descriptor of HER activity as a first approximation^{66–71}. And when ΔG_H is closest to thermal-neutral, the HER activity is the best.

Compared with other NPM based HER electrocatalysts, MXenes has higher potential, as well as other excellent physical and chemical properties: (a) A large amount of -OH and -O groups on the surface of MXenes can establish a strong correlation with a variety of semiconductor surfaces. (b) Superior electrical conductivity of MXenes facilitates efficient charge-carrier transfer. (c) The metal sites exposed at the terminals of MXenes enable stronger redox activity than that of carbon materials. (d) Excellent hydrophilicity of MXenes ensures the adequate contact with water molecules. (e) MXenes have excellent structural and chemical stability in aqueous solutions.

In recent years, MXenes-based HER electrocatalysts have attracted increasing attention, and there have been numerous experimental and theoretical research. The MXenes have been

optimized intrinsically and extrinsically via structural engineering, from the aspects of termination modification, metal-atom doping, nanostructure fabrication, and hybridization. MXenes and MXene-based composites as HER electrocatalysts display potential progress in replacing Pt-based catalysts (Table 2).

Termination modification

Termination modification of MXenes is considered beneficial for enhancing HER performance, via improving the conductivity and surface termination⁷¹. It is well recognized that the termination modification of MXenes can optimize the electronic structure and promote HER activity constitutionally. In recent years, termination modification of MXenes has been widely investigated with experimental and theoretical studies.

2D MXenes with O*/OH* terminal groups exhibited metallic properties experimentally, thus supporting excellent charge transfer⁷². Consistent with the experimental results, the surface Pourbaix diagrams also proved that MXenes with O*/OH* terminal groups show the best surface chemical stability. The performance of O*/OH*-terminated MXenes was also optimized, manifested as dramatically improved exchange current and promoted hydrogen evolution (Fig. 7a–b). The ΔG_H was calculated, demonstrating that surface oxygen atoms were active sites for the HER. These surface oxygen atoms promoted the interaction between H* and 2D MXenes. Further study demonstrated that the HER process of O-terminated MXenes followed the Heyrovsky mechanism. The HER activity of MXenes with diverse surface groups (-O, -OH, -F) was exploited (Fig. 7d–f)⁷³. The O-terminated surface was much more effective than OH- and F-terminated surface. Above studies have proved that the catalytic activity of 2D MXenes based HER catalysts can be adjusted with termination modification.

The theoretical analysis has been further performed. Ling et al.⁷⁴ calculated the electron numbers of O in all sites of the 7 types of M'M''CO₂. The potential site with high HER activity was identified, including O_{Ti2V1} and O_{V2Ti1} sites in TiVCO₂, and O_{W2Mo1} sites in WMoCO₂. Their HER performance was further evaluated by calculating ΔG_H values (Fig. 7c). O_{Ti2V1} and O_{V2Ti1} sites were appropriate for HER. Further, the calculated $|\Delta G_H|$ value was 0.01–0.06 eV for O_{Ti2V1}, which was comparable to Pt (111) surface (~0.09 eV).

Several other studies on termination modification have been performed. Jiang et al.⁷⁵ designed an efficient HER electrocatalyst based on the ultrathin O-functionalized Ti₃C₂ MXenes. The counterpart F-functionalized MXenes on the basal plane was detrimental to HER, depressing hydrogen adsorption kinetics. Ti₃C₂O_x was prepared by dispersing Ti₃C₂T_x in KOH aqueous solution, and the F-termination was reduced with OH groups⁷⁶. Then, the Ti₃C₂(OH)_x was calcinated under 450 °C in Ar atmosphere, and the OH groups would be transformed into O-terminal group via dehydration reaction. As shown in Fig. 7g–h, Ti₃C₂O_x nanosheets was proved to be a superior HER electrocatalyst. It provided an overpotential of 190 mV at current density of 10 mA cm⁻², which was much lower than that of Ti₃C₂(OH)_x (217 mV) and Ti₃C₂T_x-450 (266 mV). Further, the Tafel slope was 60.7 mV dec⁻¹, resulted from the highly active O-sites on the basal plane of Ti₃C₂O_x MXenes. This work lays the foundation for improving the performance of MXenes-based HER electrocatalysts by modifying their surface terminal groups.

In short, the catalytic activity of MXenes in HER is influenced by the functional groups on the basal plane. For Ti₃C₂, Mo₂C, Mo₂Ti₂C₃ MXenes, higher F content on the basal plane indicated lower HER activity⁷⁷. The O-terminated Ti₃C₂ MXenes is an ideal electrocatalyst for HER^{70,73}. Thus far, MXenes with other surface groups (such as -S, -Cl, -Br) have been synthesized, but their HER performance has not been discussed.

Fig. 7 MXenes-based HER electrocatalysts optimized by modifying their surface terminal groups. **a** Schematic of hydrogen evolution of MXenes with O-termination. **b** The correlation of exchange current (i_0) and ΔG_H . Copyright 2016, American Chemical Society. **c** Calculated free-energy diagram of HER at equilibrium potential for O_{Ti2V1} , O_{V2Ti1} , and O_{W2Mo1} sites. Copyright 2016, American Chemical Society. **d** The structure model for a $4 \times 4 \times 1$ O-terminated Ti_3C_2 supercell. **e, f** The calculated free-energy diagram of HER at the equilibrium potential on the surface of a $2 \times 2 \times 1$ O-terminated Ti_3C_2 supercell, and the referenced Pt, MoS_2 , and WS_2 . Copyright 2017, Springer Nature. **g** Polarization curves of E- $Ti_3C_2T_x$, E- $Ti_3C_2(OH)_x$, E- $Ti_3C_2O_x$, E- $Ti_3C_2T_x$ -450, and 20 wt% Pt/C on the GC electrode. **h** Tafel slopes. Copyright 2019, WILEY-VCH.

Metal-atom doping

Most recently, atoms have been doped into 2D materials like MoS_2 ⁷⁸, graphene⁷⁹, graphdiyne⁸⁰, etc. to improve the performance of HER electrocatalysts, from the aspects of tuning the electronic structure, modifying the elemental composition, and handling surface chemistry^{81,82}. In the 2D material lattice and coordination environment, the single-atom catalysts can stabilize single metal atoms with strong covalent bonds, which can function as active sites for HER (Fig. 8a)⁸³. Inspired by this phenomenon, the HER catalytic activity of MXenes can be enhanced experimentally and theoretically by confining single metal atom.

The structural and computational model of transition metal (TM)-promoted V_2CO_2 was established (Fig. 8b)⁸⁴. Four surface sites with different activity could be obtained under varied hydrogen coverage rate. These sites were labeled as T_0 , T_1 , T_2 , and T_3 , in which 'T' indicated 'top site of surface O atom' and the subscript was the number of surrounding V atoms that connected to active O atom and the promoter atom. By using first-principles

calculation (Fig. 8c), ΔG_H was generally greater in TM-promoted V_2CO_2 , compared to that of pristine V_2CO_2 . The bonding strength of H-O on the surface of the TM- V_2CO_2 can be reduced, thus improving HER performance. Moreover, by adjusting the adsorption concentration of TM atoms on the surface, the catalytic activity can also be effectively regulated. Most importantly, ΔG_H of T_3 (25% TM-Ni), T_0 (16.7% TM-Fe), T_1 (16.7% TM-CO), T_1 (16.7% TM-Fe), and T_2 (12.5% TM-CO) was only -0.01 , -0.04 , -0.05 , 0.03 , and -0.03 eV, respectively, showing performance superior to commercial Pt/C (≈ 0.09 eV)⁸⁵.

The effects of metal atoms (Ir, Os, Re, Rh, Fe and Zn) modification on HER activity were also explored, with Ti_3CNO_2 as a model (Fig. 8d)⁸⁶. On each side of Ti_3CNO_2 MXenes, three O-atom sites were systematically selected (labeled as S_1 , S_2 and S_3), and the corresponding ΔG_H was calculated. All three kinds of O sites on the C-side of Ir, Rh, Zn modified system aided in the enhancement of HER activity. Further, at least one O site on the C-side of Re, Os and Fe doped Ti_3CNO_2 surface exhibited HER activity (Fig. 8e). Li et al.⁸⁷ also demonstrated that the catalytic activity of MXenes materials could be optimized by surface

Fig. 8 MXenes-based HER electrocatalysts optimized by metal-atom doping. **a** Schematic illustration of hydrogen evolution of TM-doped MXenes. **b** The structural and computational models of TM-promoted V_2CO_2 . **c** Calculated ΔG_H of V_2CO_2 with 12.5%, 16.7%, and 25% monolayer (ML) H coverage on one surface TM coverage as a function of promoter and active site⁸⁴. Copyright 2016, WILEY-VCH. **d** Top and side view of metal modified Ti_3CNO_2 MXenes. S_1 , S_2 and S_3 denote the sites for H atom adsorption sites. **e** Calculated ΔG_H on C-side of metal modified Ti_3CNO_2 MXenes⁸⁶. Copyright 2018, WILEY-VCH. **f** Top view of the slab models for describing $Mo_2TiC_2T_x-Pt_{SA}$. **g** The electrochemical exfoliation of MXenes with immobilized Pt single atoms. **h** HER polarization curves of carbon paper (CP), $Mo_2TiC_2T_x$, $Mo_2TiC_2T_x-V_{Mo}$, $Mo_2TiC_2T_x-Pt_{SA}$ and Pt/C (40%)⁸⁸. Copyright 2018, Springer Nature.

modification with TM atoms. These theoretical results provide vital insights into catalytic mechanism of TM-doped MXenes for HER. It assists in designing and applying TM-doped MXenes in electrochemical reactions.

Apart from the theoretical basis, several strategies have been developed experimentally to produce monometallic atom doped MXenes, including electrochemical exfoliation⁸⁸, pyrolysis⁸⁹, MAX precursor doping⁹⁰. A stable single-atom catalyst $Pt_1/Ti_{3-x}C_2T_y$ was prepared by using ultrathin 2D $Ti_{3-x}C_2T_y$ MXenes, which provided many Ti defect vacancies and high reduction capacity⁹¹. A strong metallic carbon bond was formed between the single atom and $Ti_{3-x}C_2T_y$. Zhang et al.⁸⁸ designed single Pt atom-MXenes catalyst ($Mo_2TiC_2T_x-Pt_{SA}$) with a high mass activity. Electrochemical exfoliation of double transition metal MXenes ($Mo_2TiC_2T_x$) was firstly performed, followed by immobilizing Pt single atoms in the Mo vacancies (Fig. 8f-g). As a result, $Mo_2TiC_2T_x-Pt_{SA}$ delivered an overpotential of 30 mV at 10 mA cm^{-2} , much better than that of the pristine $Mo_2TiC_2T_x$ and $Mo_2TiC_2T_x-V_{Mo}$ (Fig. 8h). The Density functional theory (DFT) calculations showed that the ΔG_H values of $Mo_2TiC_2T_x-Pt_{SA}$ was -0.08 eV, which was lower compared to that of $Mo_2TiC_2T_x$ (-0.19 eV) and Pt (-0.1 eV). Besides, $Mo_2TiC_2T_x-Pt_{SA}$ showed excellent stability as HER electrocatalyst, resulted from the strong interaction of Pt atoms with $Mo_2TiC_2T_x$, thus preventing the surface diffusion and coarsening. Single site

Co-substituted 2D molybdenum carbide (Mo_2CT_x ; Co) can be obtained from a Co-substituted Mo_2GaC MAX precursor⁹⁰. The Mo_2CT_x ; Co delivered an overpotential of 180 mV at 10 mA cm^{-2} , better than that of Mo_2CT_x (230 mV). The DFT result suggested that Co-substituted Mo_2CT_x promoted the adsorption of hydrogen on the MXenes surface, thus enhancing the HER kinetics.

Nanostructuring

Nanostructure architecting has been another strategy for improving HER electrocatalytic activity of MXenes, such as nanoribbons and nanodots. The MXenes with certain nanostructures possess quick electrochemical response, special electronic properties, and abundant active sites, which can be potential HER electrocatalysts. Nanostructuring expands the application scope of MXenes and assists in assembling active components.

Twelve kinds of MXenes nanoribbon systems were constructed⁹². DFT calculations revealed that the edges of MXenes nanoribbons containing metal and C(N) atom could capture hydrogen species, which can be applied as the reaction sites for hydrogen evolution with fast kinetics. These MXenes nanoribbons displayed different ΔG_H (Fig. 9a-c). Notably, the nanoribbons of Ti_3C_2 and solid solution (Ti, Nb) C showed a ΔG_H close to zero, with the Tafel barrier as low as 0.42 and 0.17 eV. Designing specific

Fig. 9 MXenes-based HER electrocatalysts optimized by nanostructure architecting. **a** Free energy diagrams for hydrogen evolution at zero potential and pH = 0 on the edges of various MXenes nanoribbons. **b** Free energy profiles for hydrogen formation on the edges of Ti_3C_2 . **c** Free energy profiles for hydrogen formation on the edges of (Ti, Nb) C MXenes nanoribbons⁹². Copyright 2018, Royal Society of Chemistry. **d** Schematic diagram for the preparation of Ti_3C_2 NFs. **e** LSV and **f** Tafel slopes of Ti_3C_2 NFs, Ti_3C_2 flakes, and Pt/C electrodes. **g** N_2 adsorption-desorption isotherm of Ti_3C_2 flakes and NFs⁹⁶. Copyright 2018, American Chemical Society.

nanostructure is an innovative strategy for enhancing the HER activity of MXenes.

Several synthetic strategies have been reported to prepare MXenes nanoribbons or nanodots, such as hydrothermal treatment⁹³, shaking treatment⁹⁴, or ball-milling⁹⁵. $\text{Ti}_3\text{C}_2\text{T}_x$ nanofibers (NFs) can also be fabricated from hydrolyzed bulk Ti_3AlC_2 and HF etching (Fig. 9d)⁹⁶. As shown in Fig. 9e–f, the obtained $\text{Ti}_3\text{C}_2\text{T}_x$ NFs exhibited high HER catalytic activity, manifested as an overpotential of 169 mV at 10 mA cm^{-2} , which was better than $\text{Ti}_3\text{C}_2\text{T}_x$ flakes (385 mV). The Tafel slope was 188 and 97 mV dec^{-1} for the $\text{Ti}_3\text{C}_2\text{T}_x$ flakes and NFs, respectively. Meanwhile, the MXenes NFs provided much higher specific surface area (up to $58.5 \text{ m}^2 \text{ g}^{-1}$) compared to that of MXenes flakes ($8.5 \text{ m}^2 \text{ g}^{-1}$), thus exposing more active sites (Fig. 9g). Hence, the high HER catalytic performance of proposed $\text{Ti}_3\text{C}_2\text{T}_x$ NFs was mainly resulted from the improved specific surface area and increased active sites.

A 3D interconnected porous framework of alkalinized Ti_3C_2 ($\text{a-Ti}_3\text{C}_2$) MXenes nanoribbons were prepared via continuously shaking Ti_3C_2 MXenes in alkalinized solution (KOH). Because of the increased interlayer spacing and narrowed nanoribbons width, the reaction kinetics and morphology stability can be improved⁹³. Such alkalization strategy can be further broadened to prepare other MXenes-based materials, which are applicable to a large family of MAX phases. Water-soluble and monolayered Ti_3C_2 MXenes quantum dots (MQDs) were prepared with hydrothermal treatment⁹⁴. Upon etching the A elements in the Ti_3AlC_2 MAX phase with 48% HF acid, bulk layered Ti_3C_2 MXenes were cut. Few-layered $\text{Ti}_3\text{C}_2\text{T}_x$ nanodots (TNDs) (2–5 nm in thickness, $\approx 6 \text{ nm}$ in size) were synthesized using ball-milling with red phosphorus (P)⁹⁵. In theory, MXenes would be increased in practice by

reducing their lateral size to the nanoscale. The surface O groups of $\text{Ti}_3\text{C}_2\text{T}_x$ would interact with P strongly and chemically, thus forming nanodots under the ball-milling shear force. Notably, almost all raw $\text{Ti}_3\text{C}_2\text{T}_x$ was converted to TNDs, and the sizes can be controlled by ball-milling with other elements, including carbon, sulfur, and silicon.

In short, MXenes nanostructures can directly affect the HER activity, from the aspects of catalytic process, active sites, and charge transfer^{97,98}. Several methods have been reported to construct nanostructures of MXenes, from 1D to 3D architectures^{99,100}. More than 30 kinds of MXenes with various nanostructures have been experimentally synthesized and applied as catalysts. These MXenes are promising candidates for HER electrocatalyst.

Hybridization

The hybridization of MXenes with other active materials has been demonstrated to synergistically promote HER activity, such as chalcogenides^{101–110}, layered hydroxides¹¹¹, phosphides^{112,113}, metal nanoparticles/alloys^{114–121}, carbides^{122,123} and even metal-free black phosphorus¹²⁴. The ΔG_{H} of MoS_2 can be precisely tuned¹²⁵ by integrating with various 2D materials, such as graphene, h-BN, phosphorene, transition metal dichalcogenides, MXenes, and their derivatives. The catalytic performance of MoS_2 can be enhanced at low S vacancy concentration with first-principles calculations. It was worth noting that the optimal free energy $\Delta G_{\text{H}} = 0$ could be realized at S vacancy concentration as low as $\sim 2.5\%$, and there was high porosity and tunability in $\text{MoS}_2/\text{MXenes-OH}$ heterostructures.

Fig. 10 MXenes-based HER electrocatalysts optimized by hybridization. **a** Illustration of the ‘nanoroll’-like MoS₂/Ti₃C₂T_x composite. **b** Polarization curves and **c** Tafel plots of MoS₂/Ti₃C₂T_x composite, pristine MoS₂ and Ti₃C₂T_x nanosheets¹⁰¹. Copyright 2019, Elsevier. **d** In-situ X-ray absorption spectroscopy. **e** HER polarization curves at 2 mV s⁻¹ in H₂ saturated 0.1 M HClO₄. **f** Specific activity of the Pt/Vulcan and Pt/Ti₃C₂T_x catalysts, which was normalized by H₂ chemisorption at -60 °C¹¹⁷. Copyright 2019, American Chemical Society. **g** Atomic configuration of Co/Ni replaced Ti atom on Nb-doped monolayer Ti₃C₂O₂ and the three different O sites for H* adsorption. **h** ΔG_H for H* adsorbed at active site on M-doped Ti₃C₂O₂ monolayer. **i** HER polarization curves of the NiCo@NTM nanohybrids, Ni@NTM nanohybrid, NTM, and 10% Pt/C in 1 M KOH¹¹⁴. Copyright 2019, WILEY-VCH.

Recent experimental studies have also confirmed above findings. As displayed in Fig. 10a, a quick-freezing method was designed to prepare the ‘nanoroll’-like MoS₂/Ti₃C₂T_x composite¹⁰¹. After liquid nitrogen-freezing and annealing, a hierarchical MoS₂/Ti₃C₂T_x can be obtained, with a diameter of ~200 nm and length of several microns. The rapid freezing functioned in rolling Ti₃C₂T_x nanowires and forming vertically oriented MoS₂ microcrystals. This MoS₂/Ti₃C₂T_x composite provided abundant reaction sites and promoted charge transfer in electrocatalytic reactions. Good catalytic performance was achieved, manifested as an initial overpotential of 30 mV and a low overpotential of 168 mV at 10 mA cm⁻². The Tafel slope was 70 mV dec⁻¹. In addition, the exchange current density was increased by over 25 times compared to that of MoS₂ (Fig. 10b-c). By mounting a few carbon coated MoS₂ nanocrystals on the carbon stabilized Ti₃C₂ MXenes, the spontaneous oxidation can be hindered⁹³. The obtained MoS₂/Ti₃C₂T_x@C nanocrystals show superior HER catalytic activity and stability in acidic solution. The overpotential was determined as 135 mV at 10 mA cm⁻², with a Tafel slope of 45 mV dec⁻¹. Besides of MoS₂, the MXenes can also be coupled with other transition metal chalcogenides for enhancing HER activity, including NiS₂¹⁰⁶, NiSe₂¹⁰⁵, VS₂¹⁰² and MoSe₂^{107,109}.

Most remarkable, MXenes can greatly promote HER activity by supporting metal nanoparticles (NPs) and binary alloys. Li et al.¹¹⁷ reported Pt₃Ti intermetallic compound (IMC) NPs on Ti₃C₂T_x MXenes, in which Pt interacted with Ti on the Ti₃C₂T_x MXenes via in-situ co-reduction. The in-situ X-ray absorption spectra showed

that Pt atom was transformed to IMC with increased temperature (Fig. 10d). The obtained Pt/Ti₃C₂T_x-550 showed excellent performance, requiring a potential of only 32.7 mV at 10 mA cm⁻² (Fig. 10e). The mass activity and specific activity of Pt/Ti₃C₂T_x-550 was better than that of Pt/Vulcan (Fig. 10f). Wang et al.¹²¹ synthesized a class of composite FeNi@MXene (Mo₂TiC₂T_x)@nickel foam (NF) through introducing Fe²⁺ ions and in-situ combining with surface nickel atoms on nickel foam. FeNi@Mo₂TiC₂T_x@NF exhibited high HER activity with an overpotential of 165 mV at 10 mA cm⁻² due to the synergetic effect of Mo₂TiC₂T_x and FeNi nanoalloys. Du et al.¹¹⁴ reported a Ti₃C₂T_x MXenes based hybrid material modified by doping Nb and surface Ni/Co alloy (Fig. 10g). DFT calculation show that, after Nb doping, the Fermi energy level was shifted toward the conduction band, thus improving the conductivity. In addition, Ni/Co alloy modified M-H bond on the surface of catalyst, thus adsorbing the H with the lowest ΔG_H (Fig. 10h). The synthesized Ni_{0.9}Co_{0.1}@NTM (Nb-doped Ti₃C₂T_x) hybrid exhibited excellent HER activity, requiring an overpotential of only 43.4 mV at 10 mA cm⁻² (Fig. 10i). Further, long-term stability can be obtained.

CONCLUSION AND OUTLOOK

The development of NPM, environmentally friendly and high-performance electrode materials is significant for energy storage, conversion, and utilization. Because of the large surface area, excellent metallic conductivity, and good hydrophilicity, MXenes

Fig. 11 Strategies for optimizing the MXenes-based HER electrocatalysts. Schematic diagram summarizing different approaches for optimizing the MXenes-based HER.

have broad prospects as electrode material^{126–128}. This review has focused on the synthesis strategies and application advances of MXenes as electrocatalysts for HER. First, the synthesis methods of MXenes are summarized, including alkali treatment, fluoride etching, electrochemical etching, and water-free etching. It should be noted that different etching environments will generate different morphology and adjustable surface chemistry of layered MXenes products. Thus, appropriate methods should be selected according to our research objectives. Then promoting HER performance via termination modification, metal-atom doping, nanostructure architecting and hybridization have been systematically introduced (Fig. 11). Although extensive progress has been made in developing MXenes-based electrocatalysts during the past few decades, it remains challenging to develop highly active electrocatalysts that are superior to Pt-based materials and can be commercialized. For instance, (a) Etching in aqueous solution (fluoride etching, alkali etching, electrochemical etching) is detrimental to obtaining high-quality MXene because the dissolved oxygen gas in aqueous etchants induces extra structural defects to MXene sheets and promotes their degradation into TiO_2 . (b) Non-aqueous etching by molten salt requires high temperature, making it difficult to industrialize. (c) The surface functional groups of MXene are still difficult to tune, for which depend on the synthesis method. Based on this, the catalytic mechanism remains controversial due to complex surface environment. (d) The yield of MXene nanostructure is low, and can limit the practicality of MXenes on a large scale.

Based on the above synthesis and modification strategies, the hydrogen production efficiency of MXenes-based electrocatalysts in the future can be improved from the following aspects:

- (a) **Synthesizing various new MXenes.** Based on newly discovered Mo_4VAlC_4 MAX phase and corresponding Mo_4VC_4 MXenes¹²⁹, synthesizing various new MXenes with five or even more transition metal atomic layers in the laboratory may present excellent HER performance in the future, such as Mo_5C_4 , Mo_4TiC_4 . Based on newly reported W-based in-plane chemically ordered $(\text{W}_{2/3}\text{R}_{1/3})_2\text{AlC}$ ($\text{R} = \text{Gd}$, Tb , Dy , Ho , Er , Tm and Lu) MAX phases and their 2D $\text{W}_{1.33}\text{C}$ MXene derivatives¹³⁰, discovering more new M, A, X layer

elements may improve the HER activity of MXenes obtained by etching MAX.

- (b) **Modified MAX phase synthesis.** Based on the fact that incomplete etching and a small amount of residual A atoms during etching MAX can increase HER activity of MXenes, adding the compounds containing excessive transition metal M, or excessive A atom, or excessive C, N or CN during the synthesis of MAX may improve the HER performance of MXenes obtained by etching MAX, such as $\text{Mo}-(\text{Mo}_4\text{AlC}_3)$, $\text{W}-(\text{W}_3\text{AlC}_2)$, $\text{Al}-(\text{Mo}_4\text{AlC}_3)$, $\text{Zn}-(\text{V}_4\text{ZnC}_3)$, $\text{C}-(\text{W}_4\text{AlC}_3)$, $\text{N}-(\text{Ti}_2\text{AlN})$, $\text{CN}-(\text{Ti}_3\text{AlCN})$.
- (c) **Pre-processing of the MAX phase.** Treating MAX by various methods, such as hydrolysis, ball milling and sonication before etching MAX may improve the HER activity of obtained MXenes. Coupling MAX with other active materials and a subsequent etching process may improve HER performance, such as MoS_2 , C_3N_4 .
- (d) **Optimizing etching process.** (i) Etching two or more MAX simultaneously, doping metal and etching MAX simultaneously may improve the HER activity of MXenes during etching MAX. (ii) MXenes with some surface terminal groups ($-\text{Cl}$, $-\text{Br}$, $-\text{Te}$, $-\text{Se}$, $-\text{S}$) obtained by molten salt (Lewis acid) etching may provide higher HER activity than those with $-\text{F}$, $-\text{O}$, $-\text{OH}$ after above optimization strategies, thus discovering more new surface terminations of MXenes may improve HER activity, such as $-\text{I}$, $-\text{Po}$. (iii) The novel MXenes materials prepared by non-MAX phase precursors may present innovative HER properties. (iv) Developing novel MXene nanostructures by reducing the lateral size to nanoscale, and further combining these nanostructures with 3D open porous network or other high-HER active materials may enhance the HER properties.

DATA AVAILABILITY

Data sharing was not applicable to this paper, as no original data were generated for this review.

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AUTHOR CONTRIBUTIONS

J.J. directed and supervised the project. S.B. drafted the manuscript with inputs from M.Y., J.J. and S.L. All authors discussed and modified the manuscript at all stages.

COMPETING INTERESTS

The authors declare no competing interests.

ADDITIONAL INFORMATION

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