MXene and MBene as efficient catalysts for energy conversion: roles of surface, edge and interface

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Abstract

MXenes and MBenes emerge from a large family of two-dimensional (2D) transition metal carbides, nitrides, carbonitrides, and borides and have drawn tremendous attention in recent years. They possess diverse elemental compositions, surface terminations and geometrical structures, and exhibit many fascinating physical and chemical properties. Specifically, these 2D compounds hold great promise for renewable energy applications owing to their superior electrical conductivity, high hydrophilicity, rich surface chemistry, and outstanding stability. In this perspective, we present a brief overview about the catalytic properties of MXenes, MBenes and MXene based heterostructures for typical electrochemical reactions. The roles of surface, edge and interface of these 2D nanostructures in energy conversion are highlighted from a theoretical point of view. Challenges and outlooks for future research are also outlined.

1. Introduction

MXenes, early transition metal carbides, carbonitrides and nitrides, form an important family of two-dimensional (2D) materials. They have a hexagonal close-packed structure with chemical formula of $M_{n+1}X_n$ ($M =$ early transition metal element; $X =$ C, N; $n = 1–3$) (as shown in figure 1(a)). MXenes are commonly synthesized by etching the A elements from their corresponding bulk MAX phases using chemicals, such as hydrofluoric acid, ammonium hydrogen bifluoride, or an acidic solution of fluoride salts. Thus their surfaces are inevitably terminated by O, OH and/or F atoms [1]. So far, numerous kinds of MXenes have been fabricated in laboratory (e.g. Ti$_2$C, V$_2$C, Mo$_2$C, Ti$_3$C$_2$ and Nb$_4$C$_3$), and MXenes with more than one M element also exist in either solid solutions or ordered phases [2]. Owing to the large surface area, hydrophilic nature, superior electrical conductivity, and outstanding structural and chemical stabilities, MXenes hold great promise for energy applications, including supercapacitors [3], Li ion batteries [4], water splitting for hydrogen production [5], and other catalytic processes [6–8].

Theoretical efforts have also been devoted to understanding the physical and chemical properties of MXenes with different chemical compositions. It has been shown that pristine MXenes are all metallic. Upon surface functionalization, some MXenes such as $M_2$CO$_2$ (M = Sc, Ti, Zr, Hf) become semiconducting [9]; $M_2$CO$_2$ (M = Mo, W) and $M'$$_2$M''$_2$C$_2$O$_2$ ($M' =$ Mo, W; $M'' =$ Ti, Zr, Hf) are topological insulators, and $M'_2$M''$_2$C$_2$O$_2$ are topological semimetals [10, 11]. Moreover, many of the pristine MXenes are intrinsically magnetic. For example, Ti$_2$C, Ti$_3$N and Cr$_2$C exhibit half-metallic ferromagnetism, while V$_2$C and Cr$_2$N are antiferromagnetic [12, 13]. Their magnetic states are highly tunable under external strains. Besides electronics and spintronics, potential applications have been proposed for MXenes in optics [14, 15], thermoelectric devices [16, 17], sensors [18], and catalysts for a variety of chemical reactions [19–23]. In particular, MXenes of various compositions have been predicted as promising heterogeneous catalysts for nitrogen fixation [24], CO$_2$ separation from methane [25], and water dissociation to promote water-gas shift reaction [26].
Recently, the MAX phases have been extended to the ternary transition metal borides (namely, MAB phase \[27, 28\]), which in turn have aroused significant interests to explore the corresponding 2D transition metal borides, i.e. MBenes. Density functional theory (DFT) calculations have predicted a number of stable MBenes, such as Mo\(_2\)B\(_2\), Fe\(_2\)B, MnB, Nb\(_2\)B\(_2\), and Ta\(_3\)B\(_4\), which have diverse structures including hexagonal, orthogonal and tetragonal phases and different stoichiometric ratios of metal and boron atoms \[27, 28\] (as displayed in figure 1(b)). Soon after the theoretical predictions, TiB, MoB and CrB MBenes were successfully fabricated in laboratory by the removal of the middle In or Al layer from the parent Ti\(_2\)InB\(_2\), MoAlB and Cr\(_2\)AlB\(_2\) solids, respectively \[29–31\]. Distinctive from MXenes, there is no evidence for the presence of functional groups on the synthetic MBene surfaces \[31\]. Potential applications have also been proposed for MBenes, such as high Curie temperature ferromagnet \[27\], electrode material for lithium ion batteries \[28\], and electrocatalysts for hydrogen evolution reaction (HER) and nitrogen fixation \[32, 33\].

Since their discovery, MXenes and MBenes as a large family of 2D transition metal compounds play a key role in renewable energy applications. The investigations on these novel 2D materials are rapidly proceeding. There have been several review articles covering the synthesis, fundamental properties, and applications of MXenes in energy storage \[2, 34–36\]. In this perspective, we present an overview on the recent progress of MXenes and MBenes as electrocatalysts for energy conversion, mainly highlighting the theoretical understanding of the intrinsic activity of MXenes, synergistic effect of MXene based heterostructures, and modulation of the catalytic properties of MBenes.

2. Intrinsic activity of MXene sheets and nanoribbons

Electrocatalytic water splitting is one of the most efficient ways for sustainable hydrogen generation. Developing efficient and low-cost catalysts for HER to replace noble metal catalysts is highly imperative for large-scale hydrogen production \[37\]. Exploiting MXenes for electrocatalysis of HER has been an interesting topic and draws extensive theoretical investigations. Ling et al explored 17 kinds of O-terminated MXenes for HER by DFT calculations \[20\]. They showed that the O atoms on MXene surfaces can adsorb H\(^+\) species and serve as the active sites for HER. Ti\(_2\)CO\(_2\) and W\(_2\)CO\(_2\) have the hydrogen adsorption free energy (\(\Delta G_{H^+}\)) close to zero, and thus are potential HER catalysts. They also established the relationship between \(\Delta G_{H^+}\) and the number of electrons gained by O atom. With the aid of this simple descriptor, alloy MXene TiVCO\(_2\) with optimal \(\Delta G_{H^+}\) was screened.

The synthetic MXenes may be covered by O, OH and F groups in turn, whose relative concentrations and distributions have significant impact on the surface properties of MXenes. Gao et al investigated the activity of MXenes covered by different functional groups \[21\]. By calculating the surface Pourbaix diagrams, they showed that Ti\(_2\)C, V\(_2\)C and Ti\(_3\)C\(_2\) are terminated by a mixture of O and OH groups, while Nb\(_2\)C and Nb\(_3\)C\(_3\) are fully covered by O atoms under standard conditions with pH = 0, p(H\(_2\)) = 1 bar, and U = 0 V versus a standard hydrogen electrode (as given in figure 2). Ti\(_2\)CO\(_2\) provides ideal binding strength with H\(^+\) species.
Figure 2. (a) Surface Pourbaix diagrams of Ti$_2$C, V$_2$C, Nb$_2$C, Ti$_3$C$_2$, and Nb$_4$C$_3$. The most thermodynamically stable states of the surface under relevant U$_{SHE}$ conditions and pH values are labeled by the terminations. (b) Free energy diagram of HER processing on Ti$_2$CO$_2$. (c) Volcano curve of exchange current ($i_0$) as a function of the average Gibbs free energy of hydrogen adsorption ($\Delta G^*_{H^*}$). This figure is reproduced from [21].

for a wide range of H$^*$ coverage and has high activity for HER, consistent with the result reported by Ling et al [20].

The activity of MXenes can be modulated by loading promoters on their surfaces. Ling et al also introduced transition metal atoms on V$_2$C MXene by O-termination for HER [22]. They showed that transition metal atoms favor locating above the hollow sites of MXene, and induce significant charge transfer between promoter atom and surface O atoms. The number of electrons gained by O atom is remarkably increased, leading to the weakening of the binding between O and H$^*$ species. They predicted optimal concentrations of 16.7% monolayer (ML), 16.7%–25% ml and 25% ml for Fe, Co and Ni promoters, respectively, which yield the highest HER activity.

Besides surface O groups as active sites, MXene edges also provide reaction centers. Yang et al investigated the role of MXene edges in electrocatalysis of HER by constructing 12 kinds of O-terminated MXene nanoribbons [23]. They showed that the top site of C atoms on the ribbon edge tends to be saturated by H$^*$ species in acid media, while the hollow site between metal atoms on the edge can serve as the reaction sites for HER with activity depending on the chemical composition of MXene and the ribbon width (as illustrated in figure 3). The armchair nanoribbons of Ti$_3$C$_2$ and solid solution (Ti, Nb)C have not only optimal $\Delta G^*_{H^*}$, but also fast kinetics for HER with a Tafel barrier down to 0.17 eV. For rational design of MXene electrocatalysts with both favorable energetics and fast kinetics for HER, the relationship between $\Delta G^*_{H^*}$ and the d band center of metal atoms in MXenes were elucidated.

The first experimental application of MXenes for HER catalysis was reported by She et al [6]. They showed that Mo$_2$C has higher activity for HER with overpotential of 283 mV at 10 mA cm$^{-2}$, compared with 609 mV for Ti$_2$C in acidic conditions. Mo$_2$C also exhibits higher stability than Ti$_2$C, maintaining high performance after 30 cycles. Their DFT calculations suggested that Mo$_2$C is covered by mixed O and OH groups at standard conditions, which endows $\Delta G^*_{H^*}$ value closer to zero than that of Ti$_2$C fully terminated by O groups. Jiang et al prepared ultrathin Ti$_3$C$_2$ nanosheets fully functionalized with O groups for HER, which indeed exhibit much higher HER activity with overpotential of 190 mV at 10 mA cm$^{-2}$ than that of Ti$_3$C$_2$ covered by OH and F groups [38]. MXene nanofibers were also fabricated by Yuan et al, which deliver
enhanced HER activity with overpotential of 169 mV compared with traditional MXene flakes, due to the more exposed active sites in the cross section [39]. These experimental observations, to some extent corroborate the aforementioned theoretical predictions of the activity of MXene surfaces and edges.

3. Synergistic effect of MXene based heterostructures

The high metallic conductivity and rich surface chemistry render MXenes excellent conducting matrix for hybridizing with other materials for electrocatalysis. The integration of MXenes, which induce strong interfacial coupling and charge transfer, can effectively activate or enhance composite materials for various electrochemical processes. Zhou et al explored the heterostructures of N-doped graphene on bare Ti$_2$C, V$_2$C, Nb$_2$C, and Mo$_2$C MXenes [40]. Their DFT calculations showed that the supported graphitic sheets provide much enhanced binding strength with oxygen and hydrogen intermediates, compared with the freestanding systems. N-doped graphene sheets on V$_2$C and Mo$_2$C exhibit remarkable activity for both oxygen reduction reaction (ORR) and HER (as presented in figure 4). The most active sites come from the hollow-site C atoms close to N dopants, having ORR overpotentials $\eta$$_{ORR}$ down to 0.36 V and $|\Delta G_{H|^*}$ only 0.04 eV. The oxygen reduction can proceed through dual reaction pathways with kinetic barriers as low as 0.20 eV, while hydrogen evolution under the Tafel mechanism involves barriers down to 1.33 eV, suggesting fast kinetics of electrocatalysis on these heterostructures.

The synergistic effect of the graphene/MXene heterostructures can be understood by the electronic coupling between two materials. The supported graphitic sheet is strongly metalized with broken $\pi$ conjugation; consequently, the $p_z$ orbitals of C atoms are partially occupied and exhibit activity. The interlayer coupling strength is governed by the work function of MXenes, and further reflected by the $p_z$ band center ($\epsilon_{p_z}$) of the supported graphitic sheet. Generally speaking, MXenes with a larger work function shift the graphene bands to deeper energies with respect to the Fermi level, leading to lower $\epsilon_{p_z}$ and stronger binding capability with the reaction intermediates. Such a structure-activity relationship has also been established for N-doped graphitic carbon materials hybridized with transition metals or transition metal compounds [41, 42], which provides a general rule for modulating the catalytic activity of carbon based materials for various reactions.

Indeed, the graphene/MXene heterostructure has been realized in the experiment. Geng et al grew high-quality and uniform Mo$_2$C MXene film in the centimeter range on a graphene template using a Mo–Cu alloy catalyst [43]. The scanning transmission electron microscopy measurement confirmed that the produced Mo$_2$C is a well-faceted and large-sized single crystal. The vertical Mo$_2$C-on-graphene heterostructure exhibits high activity for HER with overpotential of 236 mV, much enhanced compared to Mo$_2$C-only electrodes, which was attributed to the efficient graphene-mediated charge-transfer kinetics.

Later, Wu et al utilized the synergistic effect from collaborative interfaces among bimetallic cobalt-molybdenum carbide, hybridized carbon, and MXenes for experimental HER electrocatalysis [44]. Such hybrid nanostructures exhibit outstanding HER activity and long durability in all pH ranges as well as in seawater with an overpotential of 75 mV at current density of 10 mA cm$^{-2}$ and Faradaic efficiency of 98%. Their DFT calculations revealed that Co doping into molybdenum carbide not only lowers $\Delta G_{H|^*}$. of the
composite material to 0.05 eV, but also facilitates water dissociation with a reduced kinetic barrier of 0.78 eV. Both ultraviolet photoelectron spectrometer measurement and DFT calculations showed a lower work function for the bimetallic cobalt-molybdenum carbide than that of molybdenum carbide. In consistency, the alloy carbide induces less electron transfer to the hybridized carbon material and upshifts the $p_z$ band center of C atoms, which in turn results in weaker but more suitable H* binding strength for HER catalysis. These experimental and theoretical studies corroborate the $p_z$ band center and work function as useful descriptors for design and synthesis of high-performance carbon based hybrid electrocatalysts for energy conversion.

4. Catalytic properties of MBenes

Due to the electron-deficient character of boron in comparison with carbon, exotic bonding states are present in MBenes, endowing them enormous varieties of geometrical and electronic structures. Therefore, MBenes may possess distinctive properties from those of MXenes and await exploration. Sun’s group theoretically predicted several stable MBenes including Mo$_2$B$_2$, Fe$_2$B$_2$, and Cr$_{n+1}$B$_{2n}$ ($n = 1–3$) [28]. These MBenes possess ultrahigh Young’s modulus and excellent electronic conductivity. In particular, Fe$_2$B$_2$ and Cr$_4$B$_6$ were found to have optimal $\Delta G_{H^*}$ very close to zero, and thus are potential electrocatalysts for HER.

Starting from MAB solids, Jiang et al performed high-throughput screening and proposed 12 kinds of MBenes including MnB, HfB, ZrB, Au$_2$B, Mo$_2$B, Nb$_2$B$_2$, Nb$_3$B$_4$, Ta$_3$B$_4$, V$_3$B$_4$, OsB$_2$, FeB$_2$, and RuB$_2$, which have low fracture strength, and high thermal, dynamic, and mechanical stabilities [27]. Metallic ferromagnetic behavior with high Curie temperature (345–600 K) was predicted for MnB and its F– or OH– derivatives. Based on those MBenes structures, Yang et al investigated their electrocatalytic properties for nitrogen reduction reaction (NRR) by DFT calculations [33]. They showed the outstanding stability of
MBenes in the aqueous solution at ambient condition, eligible for electrochemical applications. Among the ten considered MBene systems, OsB$_2$, FeB$_2$ and RuB$_2$ have boron exposed surfaces, while the others have metal exposed surfaces. Both types of surface can serve as the active sites for NRR, owing to the co-existence of occupied and unoccupied $p$ ($d$) states for the boron (metal) atoms. Meanwhile, the HER side reaction is suppressed in most MBenes. Interestingly, the boron reaction centers provide even superior activity than the metal atoms, with much lower onset potentials ($-0.03 \sim -0.26$ V) found for FeB$_2$, RuB$_2$ and OsB$_2$. The correlation of NRR activity with work function and number of empty orbitals of MBenes were also established (as revealed in figure 5). These theoretical studies shine light on utilizing these novel 2D borides as a new category of non-precious catalysts for energy conversion.

5. Conclusion and perspective

Developing efficient and low-cost electrocatalysts for various energy conversion processes is highly desirable for the development of our sustainable society. Together, MXenes and MBenes form a large family of 2D carbides, nitrides, carbonitrides and borides with advantageous properties for the next generation of electrocatalysts. This perspective focuses on the current understanding of the activity of MXenes, MBenes, and MXenes based heterostructures for some keystone chemical reactions, such as hydrogen evolution reaction, oxygen reduction reaction and nitrogen reduction reaction. The role of surfaces and edges on the catalytic properties of these 2D compounds, mechanism of synergistic effect in their heterostructures, and the underlying structure-band structure-activity relationships have been discussed from atomistic point of view. Some relevant experimental advances are also reviewed, which collaborate with theoretical predictions to provide comprehensive knowledge for precisely modulating the electrocatalytic performance of MXenes and MBenes.
Despite of the encouraging progress achieved, several critical challenges remain to be addressed in order to promote the practical applications of MXenes and MBenes. First, the surface properties of MXenes are highly dependent on the types and concentrations of functional groups, which are inevitably present as a result of the exfoliation process. Characterization of the surface chemistry of synthetic MXenes is important, which may be assisted with computational spectroscopy to determine the exact composition of MXenes. It is also imperative to develop new synthetic procedures for achieving uniform surface terminations as well as bare MXenes in laboratory to precisely control their properties.

Second, extensive theoretical studies have predicted the superior activity of MXenes for various chemical reactions; however, very few of them have been realized in the experiment. More often, MXenes are adopted as conducting reinforcement to composite materials for electrocatalysis in laboratory, while it remains unclear whether MXenes provide any active site during the reaction. Mechanistic studies combining both state-of-the-art experimental and theoretical approaches are desired to unveil the intrinsic catalytic properties of MXenes as well as the role of MXenes in heterostructure electrocatalysts, which would be beneficial for fully utilizing them for efficient energy conversion.

Finally, compared with the booming research on MXenes, investigation on MBenes remains in an embryonic stage from both experimental and theoretical aspects. Theoretical predictions using high-throughput calculations and machine learning would lead to the expansion of the MBene family through extensive elemental combinations and guide experimental synthesis of the most promising compounds. These novel 2D borides and their possible heterostructures wait to be prepared, characterized, and exploited in depth for practical applications. We expect breakthroughs in utilizing them for renewable energy applications in the near future.

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