Recent advances in MXenes: from fundamentals to applications

Mohammad Khazaei\textsuperscript{a,∗}, Avanish Mishra\textsuperscript{b}, Natarajan S. Venkataramanan\textsuperscript{c}, Abhishek K. Singh\textsuperscript{b}, Seiji Yunoki\textsuperscript{a,d,e}

\textsuperscript{a}Computational Materials Science Research Team, RIKEN Center for Computational Science (R-CCS), Kobe, Hyogo 650-0047, Japan
\textsuperscript{b}Materials Research Centre, Indian Institute of Science, Bangalore 560012, India
\textsuperscript{c}Department of Chemistry, School of Chemical and Biotechnology, SASTRA University, Thanjavur, 613 401, India
\textsuperscript{d}Computational Condensed Matter Physics Laboratory, RIKEN Cluster for Pioneering Research (CPR), Wako, Saitama 351-0198, Japan
\textsuperscript{e}Computational Quantum Matter Research Team, RIKEN Center for Emergent Matter Science (CEMS), Wako, Saitama 351-0198, Japan

Abstract

The family of MAX phases and their derivative MXenes are continuously growing in terms of both crystalline and composition varieties. In the last couple of years, several breakthroughs have been achieved that boosted the synthesis of novel MAX phases with ordered double transition metals and, consequently, the synthesis of novel MXenes with a higher chemical diversity and structural complexity, rarely seen in other families of two-dimensional (2D) materials. Considering the various elemental composition possibilities, surface functional tunability, various magnetic orders, and large spin–orbit coupling, MXenes can truly be considered as multifunctional materials that can be used to realize highly correlated phenomena. In addition, owing to their large surface area, hydrophilicity, adsorption ability, and high surface reactivity, MXenes have attracted attention for many applications, e.g., catalysts, ion batteries, gas storage media, and sensors. Given the fast progress of MXene-based science and technology, it is timely to update our current knowledge on various properties and possible applications. Since many theoretical predictions remain to be experimentally proven, here we mainly emphasize the physics and chemistry that can be observed in MXenes and discuss how these properties can be tuned or used for different applications.

Keywords: MAX phase, MXene, Exfoliation

1. INTRODUCTION

Owing to their unique electronic structures and large surface areas, two-dimensional (2D) materials are promising candidates for many electronic and energy applications. Hence, the synthesis, properties, and applications of novel 2D materials have currently become one of the most exciting areas of interest in science and technology. Single layers of graphene, boron nitride (BN), transition-metal dichalcogenides (MoS\textsubscript{2}, WS\textsubscript{2}, etc.), and phosphorene have been successfully obtained from their bulk van der Waals layered structures [1]. Recently, it has been shown that by using a combination of chemical exfoliation and sonication, the synthesis and mass production of 2D materials from three-dimensional (3D) layered compounds with chemical bonding between the layers are also feasible [2, 3]. In this regard, it has been demonstrated that using hydrofluoric acid (HF) solutions and sonication, some members of the MAX phase family [4] can be exfoliated into 2D transition-metal carbide and nitride layers, so-called MXenes [2, 3]. During exfoliation, depending on the type of chemical environment, a mixture of F, O, or OH groups terminates the surface of MXenes [5, 6]. It should be noted that HF is not the only etchant but LiF+HCl [7] and NH\textsubscript{4}HF\textsubscript{2} [8] have also been used for exfoliation.

The applications of solid MAX phases are somehow limited to their metallic, high-temperature stabilities, and superior mechanical properties [9, 10]. However, owing to their vast compositional possibilities, MAX phases include many crystalline and numerous alloy members. When these MAX phases are exfoliated into 2D MXenes, depending on the transition metals at the surface, thickness, and surface functionality, they exhibit quite different electronic, magnetic, optical, and electrochemical properties that are rarely seen in their original MAX phases. There are many theoretical studies in the literature that predict MXenes possess excellent electronic properties and many device applications [11]. However, most of these predictions have not been realized yet. This is because many of these pre-
dictions are based on the ideal crystal structure of MXenes without any M and X atomic vacancies and with a homogeneous surface termination having one type of the F, O, or OH group. Unfortunately, the formation of such ideal MXenes is still an experimental challenge. Recently, there are some theoretical attempts to investigate the properties of MXenes with a mixture of surface functional groups [12, 13], and conversely there have been some experimental attempts to synthesize MXenes with a uniform type of attached chemical group by using temperature control [14]. Most experimental investigations have mainly focused on the excellent electrochemical behavior of MXenes for energy storage as ion batteries, gas storage, and various catalysis applications because of their large exposed surface area, hydrophilic nature, adsorption ability, and surface activities. The latest applications and developments of MXenes have been summarized in the recent review articles [11, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26].

Although most theoretical studies are conducted using ideal MXenes and are mostly performed on the basis of density functional theory (DFT), which is known to have some drawbacks related to the accurate prediction of the band gaps and van der Waals or strongly correlated interactions, the information provided by those studies is still valuable for understanding the physics and chemistry of MXenes. In this review, we first provide a solid background of the structural properties of MAX phases and MXenes, and give insights into the possibility of the exfoliation of MAX phases into 2D MXenes. We then summarize the electronic, magnetic, and optical properties of MXenes predicted from the theoretical studies. Finally, we discuss the manifestation of these properties in various applications such as the photocatalysis, electrocatalysis, chemical catalysis, ion batteries, gas storage, Schottky barriers, thermo-, ferro-, and piezoelectric applications. This review can be considered as complementary to and an update of our previous review on the electronic properties and applications of MXenes [11].

2. Crystalline MAX Phases and their 2D derivative MXenes

MAX phases are a family of solids with layered hexagonal structures and a space group symmetry of P6₃/mmc (No. 194), whose chemical compositions are traditionally known by the chemical formula Mₙ₊₁AXₙ, where n = 1, 2, or 3, “M” is an early transition metal (Sc, Ti, Zr, Hf, V, Nb, Ta, Cr, or Mo), “A” is an element from groups III–VI in the periodic table (Al, Ga, In, Ti, Si, Ge, Sn, Pb, P, As, Bi, S, or Te), and “X” is carbon and/or nitrogen [4]. As seen in Fig. 1(a), each layer of X atoms is sandwiched between two layers of transition metals and every two Mₙ₊₁Xₙ layers are interleaved with a layer of A atoms. During an acid treatment, the ‘A’ atoms are washed from the MAX phase structure, resulting in multiple layers of Mₙ₊₁Xₙ, which can be dispersed into monolayers or a few layers by using sonication. As examples, the crystal structures of M₃AX₃ and M₃X₃ are shown in Figs. 1(a) and 2(b), respectively. Inherited from the MAX phases, the 2D Mₙ₊₁Xₙ layers also have hexagonal symmetry and in analogy to graphene, which has hexagonal symmetry, they have been named MXenes. Over 70 different Mₙ₊₁AXₙ MAX phases exist experimentally. Among them, Ti₃AlC, Ti₃AlN, V₂AlC, Nb₂AlC, Ti₃AlC₂, Ti₅SiC₂, Zr₃AlC₂, Ti₅AlN₁, V₄AlC₁, Nb₄AlC₃, and Ta₃AlC₃ have already been exfoliated into Ti₃C₂, Ti₃N, V₂C, Nb₂C, Ti₅C₂, Zr₃C₂, Ti₅N₂, V₂C₃, Nb₄C₃, and Ta₃C₃ MXenes [3, 27, 28, 29, 30, 31, 32, 33].

There are many experimental observations that a solid solution of different transition metals (M' and M'')
Figure 3: Schematic atomic configurations for chemical exfoliation of Ti$_3$AlC$_2$ using HF acid, where AlF$_3$ is extracted from the crystal. (a) pristine Ti$_3$AlC$_2$ and (b) one, (c) two, (d) three, (e) four, (f) five, (g) six, and (h) seven HF molecules intercalated into Ti$_3$AlC$_2$ [45]. White, blue, orange, cyan, and pink spheres represent Ti, C, Al, F, and H atoms, respectively.

and “A” elements (A’ and A’’) or an “X” element (C and N) results in the formation of alloy MAX phases and consequently the synthesis of various alloy MXenes. In this regard, alloy TiNbC, (Ti$_{0.5}$Nb$_{0.5}$)$_2$C, (V$_{0.5}$Cr$_{0.5}$)$_2$C$_2$, Ti$_3$CN, (Nb$_{0.8}$Ti$_{0.2}$)$_4$C$_3$, and (Nb$_{0.8}$Zr$_{0.2}$)$_4$C$_3$ MXenes have already been experimentally fabricated [3, 34]. However, it has recently been shown that by the appropriate selection and stoichiometry of M and A, and X, it is possible to synthesize two types of novel MAX phases with ordered double transition metals, named oMAX and iMAX phases. oMAX phases are MAX phases with out-of-plane ordered double transition metals, M’M’’AX$_2$ and M’M’’’AX$_3$. Figures 1(b) and 2(b) show the crystal structure of M’M’’X$_2$ and its corresponding 2D M’M’’X$_2$ MXene, respectively [35, 36, 37]. Similar to the structures of traditional M$_n$AX MAX phases, the layers of transition metals in oMAX phases are occupied with only one type of M or M’ and retain the same crystallographic space group symmetry of P6$_3$/mmc. Interestingly, their corresponding M’M’’X$_2$ and M’M’’’X$_3$ MXenes have unique configurations, as seen in Fig. 2(b), such that the outer layer of the MXene consists of a transition metal M’ only and the inside layers consists of a transition metal M’’ only. Mo$_2$TiAlC$_2$, Mo$_2$Ti$_2$AlC$_3$, Cr$_2$TiAlC$_2$, and Mo$_2$ScAlC$_2$ have already been synthesized and exfoliated into their corresponding 2D Mo$_2$TiC$_2$, Mo$_2$Ti$_2$C$_3$, Cr$_2$TiC$_2$, and Mo$_2$ScC$_2$ MXenes, respectively [35, 36, 37].

iMAX phases are MAX phases with in-plane ordered double transition metals, (M’$^\prime$)$_2$M’$^{\prime\prime}$AX. Different from traditional MAX and oMAX phases, each layer of transition metals in iMAX phases contains both M’ and M’’ [see Fig. 1(c)] [38, 39, 40, 41, 42, 43, 44]. In contrast to previous MAX phases that consist of A atoms forming a hexagonal lattice, A atoms are located on a Kagome-like lattice in iMAX phases. This occurs because of the different atomic sizes in which M’ < M’’ such that the M’’ atoms cause the A atoms to deviate from the hexagonal lattice to the Kagome-like lattice [43]. The space group symmetry of iMAX phases is C2/c. Accordingly, after exfoliation, the 2D MXenes obtained from iMAX phases include two different types of transition metals in each layer of transition metals [see Fig. 2(c)]. In analogy to 2D MXenes, the 2D structures derived from iMAX phases can accordingly be called as iMXenes. The iMAX phases of (M’$^\prime$)$_2$M’$^{\prime\prime}$AX (M’ = Cr, Mo, W; M’’ = Sc, Y), and (M’$^\prime$)$_2$Zr$_{1/2}$AlC (M’ = V, Cr) have already been experimentally fabricated and most of them have already been exfoliated. However, during exfoliation process, Sc/Y and Al are dissolved, resulting in the formation of 2D M’$^{33}$C MXenes with ordered vacancies [38, 39, 40, 41, 42, 43]. It is noteworthy that (Nb$_{2/3}$ScC$_{1/3}$)$_2$AlC has also been fabricated in the solid solution form and its exfoliation results in 2D Nb$_{133}$C MXene with randomly distributed vacancies [44].

3. Exfoliation of MAX phases to MXenes

The chemical exfoliation of MAX phases is a complex process with many reaction kinetics and dynamics, which makes it difficult to model or simulate them in
The exfoliation process of MAX phases into 2D MXenes necessarily involves the elimination of the A element using an acid treatment, e.g., a HF solution. The exfoliation process of MAX phases into 2D MXenes has been investigated [47]. It was shown that by applying large tensile stress, the M–Al bonds are broken, leading to the separation of the 2D MXene sheets from the MAX phase [48]. Although MXenes are made by the chemical exfoliation of MAX phases, their synthesis through the mechanical exfoliation of MAX phases may also be possible. This is because in some of the MAX phases, their elastic constants \( C_{11} \) in the \( ab \) plane are larger than \( C_{33} \) perpendicular to the plane, which indicates that the overall bonding in the \( ab \) plane is stronger than that along the \( c \) direction [10, 48]. Therefore, if \( C_{33} \) is smaller than \( C_{11} \), it might be feasible to break the M–A–M bonds under appropriate mechanical tension without significantly damaging the M–X–M bonds [10, 46, 48]. This is an important theoretical observation because it reveals the possibility of the fabrication of MXenes by mechanical exfoliation of MAX phases [49]. To the best of our knowledge, there are no experiments on the mechanical exfoliation of MAX phases. However, it would be a promising method to achieve the large-scale production of MXenes at an extremely low cost.

The evaluation of the bond strengths of the M–A and M–X bonds is a straightforward method to determine the favorable candidates for the exfoliation to 2D MXenes. MAX phases with strong M–X bonds and weak M–A bonds are the best candidates. For this purpose, the force constants of the M–A–M bonds and the exfoliation energies are useful quantities for revealing information about the bond strength and the ease of bond breaking during the exfoliation process [46]. As an example of such analyses, the force constants of M–A, M1–X, M1–M1, M1–M2, and X–X bonds are investigated in Fig. 4. Here, M1 and M2 represent transition metals placed on the first and second layers of transition metals adjacent to the A element. The X layer is located between the M1 and M2 layers. Results have been accumulated for 82 different MAX and oMAX phases [46]. The overall trend is that shorter bonds are stronger. Interestingly, the force constants of the M1–X bonds are significantly higher than those of the other bonds. In other words, the M1–X bonds are the strongest in MAX phases. The X–X and A–A bonds are the weakest among all bonds, as shown in Fig. 4 [46].

Considering the static exfoliation energies of MAX phases into 2D MXenes for all MAX phases that have been already exfoliated experimentally, it is found that \( \text{V}_{23}\text{AlC}_2 \) has the largest exfoliation energy of 0.205 eV Å\(^{-2} \) [46]. Therefore, it is expected that MAX phases with an exfoliation energy smaller than 0.205 eV Å\(^{-2} \)
have a good chance to be exfoliated into MXenes. Based on the static exfoliation energy calculations and the force constant analyses, it was shown that over 37 crystalline MAX phases, as listed in Ref. [46], can potentially be exfoliated into 2D MXenes. These results indicate that in the family of MAX phases, there exist some members whose M−A (M−X) bonds are sufficiently weak (strong) such that they can (cannot) be broken during acid treatments. This explains why the exfoliation of some of the MAX phases into 2D MXenes is feasible experimentally.

4. Characteristics and emergent attributes of MXenes

4.1. Geometry and energetics

The crystalline structures of pristine 2D MXene systems can be simply obtained by eliminating the “A” element from the MAX phases. However, owing to the reactivities of transition metals, the surfaces of MXenes are usually terminated with a mixture of F, OH, and O. It is difficult to predict the electronic properties of MXenes using a model structure with the mixed adsorption of F, OH, and O on their surfaces. Hence, the majority of theoretical studies have been carried out using models with the uniform adsorption of one of the chemical groups on the surfaces [11] and very few using mixture of these groups [12, 13]. Although such ideal structures might be unrealistic at present, they help with the in-depth understanding of the physics and chemistry of MXenes and may guide and motivate ones to perform new experiments.

On the surfaces of MXenes, there are two types of hollow sites; the sites at which there exists no X atom available under them and the sites at which there exists an X atom available under them. Therefore, according to the relative positions of the adsorbed termination groups at the hollow sites, there are several choices for the uniform surface terminations of MXenes that should be taken into account for finding the lowest energy configurations before analyzing the electronic properties. It is noted that when F, OH, or O is adsorbed on top of transition metals on the surface, they usually move to hollow sites during the structural relaxation calculations. Therefore, it is anticipated that the termination groups are favorably adsorbed at the hollow sites. As explained in the previous section, the M−X bonds are the stiffest bonds in MAX phases. Hence, the chemical groups (F, OH, or O) are adsorbed at hollow sites, where the bonding states of the M−X bond achieve their highest occupancy [50]. Further thermodynamic simulations find that when the surfaces of MXenes are fully functionalized, they become thermodynamically more stable. This is understandable because, in various complexes and crystals, the number of ions surrounding a transition metal is often six, which results in the formation of a functionalized M2XT2 (T = F, OH, or O) MXene [51]. The dynamic stabilities of such fully functionalized MXenes have already been proved by phonon calculations [52].

Regarding the multilayer crystal structures of MXenes, similar to graphite, they may form in different stacking orders. Therefore, it is important to obtain the correct stacking order before examining the electronic structures of multilayer MXenes. The lowest energy coordinate structures of many of monolayer or multilayer MXenes functionalized with F, OH, or O can be found in the supporting information files of Refs. [51, 53]. These structures were determined based on the first-principles calculations using GGA/PBE method. However, it might be necessary to investigate the effect of van der Waals interactions in the stability of different stacking orders [54].

F, O, and OH form strong bonds with MXenes with large negative adsorption energies [51]. The different adsorption energies of F, OH, and O on MXenes can be explained by examining the effect of the octahedral crystal field, which is created by carbon and the chemical groups, on the d orbitals of the transition metal. For example, a recent study on Ti3C2T2 (T= O, F, H, OH) has shown that owing to the gener-
Figure 6: (a) Band structures of Mo$_2$HfC$_2$O$_2$ without and with the SOC [61]. (b) Edge states of nanoribbon of Mo$_2$HfC$_2$O$_2$ with zigzag edges [61]. Γ (0,0,0), M(1/2,0,0), K(1/3,1/3,0), X(1/2,1/2) are high-symmetry points of the Brillouin zone of a hexagonal structure. Fermi energy is located at zero energy.

Figure 7: Left and right panels exhibit the projected band structures of Ti$_3$CO$_2$ with hexagonal lattice and (W$_2$)$_3$Y$_{1/3}$CO$_2$ with rectangular lattice. Γ (0,0,0), M(1/2,0,0), K(1/3,1/3,0), X(1/2,1/2) are high-symmetry points of the Brillouin zone. Fermi energy is located at zero energy.

words, only the MXenes with formation energies less than that for V$_2$CO$_2$ have a chance for synthesis. Another important issue is the effect of the degradation of MXenes over time and due to the temperature, which might result in the transformation of MXenes into bulk transition-metal carbides or oxides [45, 57]. As an example, it has been experimentally observed that when 2D Ti$_3$C$_2$ is heated, it is transformed into TiO$_2$ particles enmeshed in thin sheets of graphitic carbon structures [57]. Thermodynamic analyses show that the large concentration of HF might convert Ti$_3$C$_2$ to TiF$_3$ and TiF$_4$ [45].

4.2. Electronic structures

Electronically, MXenes can be either topologically nontrivial or trivial. Few functionalized MXenes have been demonstrated to be topologically nontrivial semiconductors, e.g., M$_2$CO$_2$ (M = Mo, W), M$_2$′M″CO$_2$ (M′ = Mo, W; M″ = Ti, Zr, Hf), Ti$_3$N$_2$F$_2$, or semimetals, e.g., M$_2$′M″CO$_2$ (M′ = Mo, W; M″ = Ti, Zr, Hf) [58, 59, 60, 61, 62, 63]. In these MXenes, the spin–orbit coupling (SOC) affects the electronic structures significantly. In more detail, without including the SOC effect, the above MXenes are semimetals in which the highest valence band and lowest conduction band touch at the Γ point at the Fermi energy. These bands are dominated with the d orbitals of the transition metals. Upon including the SOC effect, their degeneracy at the Fermi energy is lifted, and a gap opens at the Γ point. For example, the band structures of nontrivial semiconductor Mo$_2$HfC$_2$O$_2$ MXene are shown in Fig. 6. They

Although the adsorption energies of F, O, and OH are large negative values and the mechanical properties improve after surface functionalization, the formation of functionalized MXenes depends on the competitive bulk phases. The calculation of the formation energies for M$_{n+1}$X$_n$O$_2$ (n = 1, 2, and 3; X = C or N) shows that all formation energies are positive values and V$_2$CO$_2$ has the highest positive value (+0.285 eV/atom) among the synthesized MXenes [56]. This can be considered as a threshold for the formation of new MXenes. In other
are called 2D topological semimetals and insulators, respectively, and their nanoribbon structures possess topologically protected conducting edge states that cross the Fermi energy. In other words, they display conducting edge states in which electrons with opposite spins propagate in opposite directions, and these edge states are robust against nonmagnetic impurities and disorder [64]. The nontrivial band topologies of these MXenes have also been confirmed by further band structure analyses and edge state calculations of their nanoribbon structures. The edge state of a zigzag nanoribbon structure of Mo2HfC2O2 is shown in Fig. 6, displaying the valence and conduction bands form a single Dirac cone point at M point near the Fermi energy. It is noteworthy that some MXenes such as Sc2C(OH)2 turn into topological insulators with the application of an electric field and charge transfer [65].

The majority of MXenes belong to the family of trivial metals, semimetals, or semiconductors. In other words, the SOC does not change their electronic structures significantly. Almost all pristine MXenes are metallic. However, upon surface functionalization, some of them become semiconducting, e.g., Sc2CT3 (T= F, OH, O), M2CO2 (M = Ti, Zr, Hf) [51], and (M′2/3M′′1/3)2CO2 (M′ = Mo, W; M′′ = Sc, Y) [66]. These MXenes become semiconducting due to the shift of the Fermi level and/or the change of the local crystal field around the transition metals. For example, the pristine M2X (X = C, N) systems are all metallic with the Fermi energy located at the d bands of the transition metals. In most MXenes, the p bands of C/N are below the d bands of the transition metals and these bands are separated by a small band gap [51]. F, OH, or O functionalization generates new bands below the Fermi energy, hybridized with the M d orbitals. Sc2CT3 (T= F, OH, O) and M2CO2 (M = Ti, Zr, Hf) become semiconducting because the Fermi energy is located at the center of the gap between the M d bands and the X p bands after functionalization [51]. The band structure of Ti2CO2 is shown in Fig. 7.

In the case of (M′2/3M′′1/3)2C (M′ = Mo, W; M′′ = Sc, Y), the Fermi energy moves to lower energies upon functionalization with oxygen. The origin of the band gaps in (M′2/3M′′1/3)2CO2 is the splitting of d-orbital bands [66] due to the crystal field around the transition metals. The nontrivial and semimetallic states significantly. Almost all pristine MXenes are metallic. However, upon surface functionalization, some of them become semiconducting, e.g., Sc2CT3 (T= F, OH, O), M2CO2 (M = Ti, Zr, Hf) [51], and (M′2/3M′′1/3)2CO2 (M′ = Mo, W; M′′ = Sc, Y) [66]. These MXenes become semiconducting due to the shift of the Fermi level and/or the change of the local crystal field around the transition metals. For example, the pristine M2X (X = C, N) systems are all metallic with the Fermi energy located at the d bands of the transition metals. In most MXenes, the p bands of C/N are below the d bands of the transition metals and these bands are separated by a small band gap [51]. F, OH, or O functionalization generates new bands below the Fermi energy, hybridized with the M d orbitals. Sc2CT3 (T= F, OH, O) and M2CO2 (M = Ti, Zr, Hf) become semiconducting because the Fermi energy is located at the center of the gap between the M d bands and the X p bands after functionalization [51]. The band structure of Ti2CO2 is shown in Fig. 7.

In the case of (M′2/3M′′1/3)2C (M′ = Mo, W; M′′ = Sc, Y), the Fermi energy moves to lower energies upon functionalization with oxygen. The origin of the band gaps in (M′2/3M′′1/3)2CO2 is the splitting of d-orbital bands [66] due to the crystal field around the transition metals. Schematics of d-band splittings by various types of crystal fields are shown in Fig. 8. In more detail, the states near the Fermi energy are t2g bands hybridized with C and O p orbitals, which split widely, resulting in finite band gaps [66]. As an example, the band structure of (W2/3Y1/3)2CO2 is shown in Fig. 7.

It is noteworthy that a NaN turbine database containing the structural and electronic information of approximately 15,000 MXenes has recently been released [67]. The chemical formula considered in this database is MM’XTT’, where M/M’ is an early transition metal, X is C or N, and T/T’ stands for 14 different termination groups such as F, OH, CN, and SCN [68]. The electronic properties have been predicted with a combination of DFT and machine learning. It has been found that as the electronegativity difference between the functional groups and the transition metal becomes larger, there is a higher chance for semiconducting MXenes [68]. It should also be noted that semiconducting MXenes can be engineered using strain [69], electric field [70], or by being placed on the other 2D systems [71].

In brief, the chance for obtaining semiconducting MXenes is higher for thin MXenes (n = 2; M2XT2 or (M′2/3M′′1/3)2XT2) than for thicker ones (n = 3 and 4). All M1X3T2 and M1X1T1T2 MXenes are metallic. In the family of ordered double transition metals, some of M′2M’′2C3 could become semiconducting because of spin-orbit interaction or magnetic ordering as will be discussed in the next section. Most of M′2M’′2C3 are metallic except for few of them that are semi-metal because of spin-orbit interaction. Generally, metallic or semiconducting behavior of multilayer MXenes is mostly inherited from their monolayers.

4.3. Magnetic states

Almost all MAX phases that have been reported to be magnetic are made of Cr and/or Mn, e.g., Cr2AlC, Cr2GeC, Cr2GaC, Cr2AlN, Cr2GaN, Mn2AlC, Mn2GaC,
Cr₂TiAlC₂, and (Cr₂/3Sc₁/3)₂AlC with various magnetic orders [36, 40, 72]. Theoretically many pristine and/or functionalized MAXenes with F, O, or OH have been predicted to be magnetic, e.g., M₂X (M = Ti, V, Cr, Mn; X = C, N), M₂MnC₂ (M = Ti, Hf), M₂TiX₂ (M = V, Cr, Mn; X = C, N), Hf₂VC₂, and Mo₃N₂F₂ [73, 74, 75, 76, 77, 78, 79, 80, 81, 82, 83].

The magnetic moments at the transition metals in the magnetic MAXenes can mostly be determined from the nominal oxidation states of the transition metals, C⁴⁺, N³⁻, F⁻, OH⁻, and O²⁻, and also by examining the coordination number of the transition metals and the number of d electrons [76, 77]. Similar to dichalcogenides, the nonbonding d orbitals in MXenes are formed near the Fermi level located between the bonding and antibonding states. Therefore, only the electrons that occupy the nonbonding d orbitals can mainly contribute to the magnetism.

As explained above, in functionalized MXenes, each transition metal is surrounded by C/N atoms and termination chemical groups, which form an octahedral cage around the transition metal, see Fig. 8. The resulting nearly octahedral crystal field splits the t₂g orbitals of the transition metal into the t₂g (dₓ²−z², dₓz, and dᵧz) and e_g (dₓ²−ᵧ², and dₓz) orbitals. Because of the orbital shapes, the e_g-orbital manifold is energetically higher than the t₂g-orbital manifold. Therefore, electrons occupy first the t₂g orbitals before entering the e_g orbitals. Various magnetic behaviors of MXenes are expected because of the different numbers of available electrons of the transition metals and the different electron configurations of the d orbitals [76]. For example, a Cr atom has six valence electrons. The nominal oxidation state of Cr is +3 in Cr₂CF₂ because, in this structure, each Cr atom donates two electrons to the neighboring C atom and one electron to the neighboring F atoms. Therefore, three electrons remain on each Cr atom that, according to Hund’s rule, fill the t₂g orbitals with the maximum spin, generating a magnetic moment of 3μ_B. Depending on how strongly the majority and minority spin bands split, the magnetic MXenes become metallic, semiconducting, or a half-metal [73, 74, 75, 76, 77, 78, 80]. For example, Cr₂CF₂ is a semiconducting MXene [76].

Recent systematic calculations on M₂N (M = Ti, Cr, Mn) found that various magnetic orders (ferro-, anti-ferro, or ferri) with different magnetic interactions (Ising, XY, or Heisenberg type) can be controlled through the strength of spin-orbit coupling, using different transition metals M, and the degree of localization of electrons, changed via the surface termination with electronegative elements (e.g. F and O) or chemical groups (e.g. OH) [80], as schematically shown in Fig 9(a).

Among the magnetic MAX phases, only Cr₂TiAlC₂ has been exfoliated into Cr₂TiC₂ [36]. Interestingly, all members of Cr₂TiC₂T₂ (T= H, F, O, OH) are semiconductors independently of the termination group [81]. It is noteworthy that the majority of magnetic MXenes have anti-ferromagnetic ground states except for some of the Mn-based ones, which are ferromagnetic [81]. Furthermore, the magnetic and electronic states of M₂X MXenes can be engineered by strain [73]. More recently, as shown in Figs. 9(b) and 9(c), due to the spin-orbit coupling, Hf₂VC₂F₂ was predicted to exhibit in-plane noncollinear 120° magnetic order [83].

Figure 9: (a) Various spin states of M₂N (M = Ti, Cr, Mn) according to spin-orbit coupling and electron localization effect [80]. (b) Side view of 2D Hf₂VC₂F₂. (c) Top view of the ab lattice structure formed by V atoms only in 2D Hf₂VC₂F₂. Arrows indicate the spin patterns at V atoms, displaying 120° noncollinear anti-ferromagnetic order [83].

4.4. Photonic properties

Various optical properties of materials such as the transmittance, absorption, reflectivity, refractive index, and energy loss can be predicted theoretically through an investigation of the real and imaginary parts of the complex dielectric constant, ε(ω) = ε₁(ω) + iε₂(ω), as a function of the photon wavelength or frequency ω. The real part ε₁(ω) [imaginary part ε₂(ω)] of the optical dielectric function is obtained using the Kramers–Kronig transformation (via the sum of the interband transitions from the occupied to unoccupied states allowed by the electric-dipole interaction) [84]. For instance, the photon absorption coefficient is evaluated as I(ω) = √2ε₀[ε₁(ω)² + ε₂(ω)² - ε₁(ω)]¹/², indicating that larger ε₂(ω) results in better photon absorption.

As the electronic characteristics of MXenes change upon surface termination, their optical properties are accordingly affected. For example, as shown in Fig. 10(a), upon functionalization of Ti₂C₂ with F, OH, and O, the real part ε₁(ω = 0) of the static dielectric constant slightly decreases, but it does not change drastically. At ω ≠ 0, however, ε₁(ω) increases with functionalization [85]. As seen in Fig. 10(a), O-terminated Ti₂C₂
Figure 10: (a) Real ($\varepsilon_1$) and imaginary ($\varepsilon_2$) parts of the dielectric constant versus frequency $\omega$ for pristine and F-, OH-, and O-functionalized Ti$_3$C$_2$ MXenes [85]. (b) In- and out-of-plane $\varepsilon_2(\omega)$ (indicated by $\varepsilon_{xy}$ and $\varepsilon_{zz}$, respectively) for O-functionalized Ti, Zr, and Hf MXenes [87]. (c) $\varepsilon_2(\omega)$ for Sc$_2$CO$_2$ and Nb-doped Sc$_2$CO$_2$ without and with 3% uniaxial and 9% biaxial strain [88].

exhibits prominent peaks at frequencies below those of visible light for $\varepsilon_1(\omega)$ as compared to the F- and OH-functionalized MXenes. Further, because of the similar electronic structures of F- and OH-terminated Ti$_3$C$_2$, $\varepsilon_2(\omega)$ exhibits similar behavior at all energies [86]. It is observed that in the visible light spectrum, the light absorption ability of O-terminated Ti$_3$C$_2$ is relatively better, i.e., larger $\varepsilon_2(\omega)$, than that of pristine, F-terminated, or OH-terminated MXenes. This is attributed to the formation of O states close the Fermi energy.

Further calculations reveal that the dielectric function tensor of MXenes is anisotropic along the in-plane and out-of-plane direction, analogs to their crystal structure. As shown in Fig. 10(b), the calculated $\varepsilon_2(\omega)$ for O-functionalized M$_2$C (M=Ti, Zr, Hf) with semiconducting properties [51] displays peaks in the visible light region. Among these MXenes, Ti$_2$CO$_2$ with two peaks at energies around 1.5 and 3.0 eV possesses the highest absorption efficiency [87], and thus can be considered as a promising candidate for applications in optical devices. However, Ti$_2$CO$_2$ does not absorb light below 1 and 2.3 eV in the in- and out-of-plane directions, respectively, because of the different reflectivities of 12% and 6%. Interestingly, the reflectivity is affected by the layer thickness and is higher for Ti$_3$C$_2$Ti$_2$ (T=F, OH, O) as compared to Ti$_2$CT$_2$ [86].

Similar to O-functionalized M$_2$C (M=Ti, Zr, Hf), Sc$_2$CO$_2$ is also a semiconductor. As shown in Fig. 10(c), $\varepsilon_2(\omega)$ of the Sc$_2$CO$_2$ has a small peak at 3.3 eV (the same value as its band gap), which results from the electron transition from the C $p$ orbitals to the Sc $d$ orbitals. By replacing one Sc atom with a Nb atom (ScNbCO$_2$), a new peak appears at 1.9 eV, which is due to the reduction of the band gap as large as 1.89 eV [88]. Furthermore, the positions of the absorption peaks can be tuned by applying stress [see Fig. 10(c)]. It is also shown that Sc$_2$CO$_2$ exhibits in- and out-of-plane polarization anisotropy, implying the application of the O-functionalized Sc-based MXenes for newly developed polarization-driven photovoltaics [89].

Recently, many photonic-based applications have been developed for MXenes [25]. For example, some MXenes such as V$_2$CT$_x$ (T = F, OH, O) with having absorption in the range of 500 to 2700 nm and high conductivity have been utilized as conductive transport electrodes [90]. Ti$_3$C$_2$T$_x$ with almost full (84%) light-to-water evaporation efficiency has the potential for application in photothermal evaporation systems [91]. Some MXenes show nonlinear light absorption applicable for optical switching devices [25].
4.5. Surface properties

The work function, defined as the difference between the Fermi level and the vacuum potential, is one of the useful surface characteristics of materials that are also used for the purpose of device applications. The work functions of pristine MXenes and MXenes functionalized with F, OH, and O are estimated to be in the ranges of 3.3−4.8, 3.1−5.8, 1.6−2.8, and 3.3−6.7 eV, respectively [92]. OH-terminated MXenes can be considered as ultralow work function materials. The change in the work function of MXenes after functionalization with respect to pristine MXenes, \( \Delta W \), can be explained in terms of the change in the surface dipole moments \( \Delta P \) [92, 93]. It is found that \( \Delta W \) and \( \Delta P \) have a linear correlation [92, 93] (see Fig. 11). The change in the surface dipole moments after surface functionalization results from i) the charge transfer and redistribution between the surface and the chemical groups, ii) the structural relaxation caused by the chemical groups, and iii) the polarity of the group [92]. Considering their work function properties, MXenes can be used to construct Schottky-barrier-free contacts with other 2D semiconductors, in which all OH-terminated (some O-terminated) MXenes can act as electron (hole) injectors [93]. It is noted that the above trends in the work functions of functionalized MXenes are independent of their thickness \( n = 1–3 \) [92]. Interestingly, the recent studies on Ti\(_3\)C\(_2\)O\(_x\)F\(_y\)(OH)\(_z\) with mixtures of surface terminations have shown that the ultralow work function of fully OH terminated MXenes can be attained by 60% OH termination on the surface [12].

Like many other 2D systems, e.g., graphene, BN, and MoS\(_2\), nearly free electron (NFE) states appear in MXenes in the spatial region above the surfaces toward the vacuum [94]. These states have parabolic bands with respect to the wave vector and generally appear at high energies above the Fermi energy and generally are not accessible except by applying electric field. Energetically, the NFE states in O- and F-terminated MXenes also appear at high energies above the Fermi energy. However, in the case of the OH termination, the NFE states appear near the Fermi energy, and for some of the OH-terminated MXenes, they are partially occupied by electrons. Because of the positively charged nature of the H atoms in OH-terminated MXenes, their surface potentials are shallow with an extended tail at energies near the Fermi energy, but they are very deep in O- or F-terminated MXenes [94]. Hence, the NFE states in OH-terminated (F- or O-terminated) MXenes can be found at energies near (above) the Fermi energy.

The NFE states are formed spatially above the surface and do not have any weight when they are projected onto the atomic orbitals of the compositional elements. However, the existence of partially occupied NFE states can be observed by visualizing the electron localization function (ELF). Figure 12 shows that a uniform electron gas exists on top of the hydrogen atoms (ELF = 0.4) above Ti\(_3\)C\(_2\)(OH)\(_2\). This implies that the OH-terminated MXenes with partially occupied NFE states...
Figure 13: The calculated energy barrier using nudged elastic band (NEB) method for switching polarization of ferroelectric Sc$_2$CO$_2$ from +P, to −P [89]. The z-axis is normal to the surface. The ferroelectric (F) states of Sc$_2$CO$_2$ are switched through an intermediate antiferroelectric (AF) state, in which the polarization is almost zero. The arrows indicate the direction of the polarizations.

can be highly sensitive to adsorbents. Therefore, they can be used for selective gas sensors [94] and heavy-element purification applications [95]. For example, as shown in Fig. 12, upon Pb atom adsorption, the NFE states of Ti$_3$C$_2$(OH)$_2$ disappear [95]. It is interesting to note that the location of NFE states relative to the Fermi energy can be tuned by either surface charges [96] or applied electric filed [97]. NFE states can contribute to electron transport [94] and surface catalytic properties. NFE states can be observed by X-ray photoelectron spectroscopy measurements [96]. The location of NFE states in energy is almost independent of the thickness of MXenes (n = 1–3). The NFE states on OH-terminated MXenes disappear when the OH-terminated MXenes are sandwich between other 2D systems such as graphene and multilayer MXenes because of the surface potential changes.

5. Applications of MXenes

5.1. Ferroelectricity

Noncentrosymmetric 2D semiconductors can exhibit ferroelectricity and/or piezoelectricity owing to their polar structures. A ferroelectric material is a polar system whose polarity can be reversed by applying an electric field. Among MXene family members, Sc$_2$CO$_2$ has uniquely in- and out-of-plane polarizations. This is due to the asymmetric occupation of O atoms on the surfaces of Sc$_2$C; on one side of the surfaces, they are adsorbed at the hollow site at which no C atoms available under them and on the other side of the surfaces, the O atoms are adsorbed at hollow sites at which C atoms are available under them. Sc$_2$CO$_2$ possesses an out-of-plane polarization of 1.60 µC/cm$^2$ with respect to its nonpolar phase [89]. The height of the energy barrier for switching from the ferroelectric phase to the anti-ferroelectric phase is 0.53 eV per formula unit, as shown in Fig. 13, which is sufficiently high for room-temperature device applications [89]. Interestingly, although Sc$_2$CO$_2$ is a semiconductor with a band gap of 1.91 eV, bilayer is of this material is a semimetal, where 2D electron and hole gases exist on the opposite sides of the surfaces [89].

More recently, it has also been reported theoretically that multiferroelectricity can be achieved in ordered-double transition metal MXenes, e.g., in Hf$_2$VC$_2$F$_2$, where the helical spin states [see Figs. 9(b) and 9(c)] generate an electrical polarization on the surface [83].

Table 1: Calculated relaxed-ion piezoelectric stress ($e_{11}$ in $10^{-10}$ Cm$^{-1}$) and strain ($d_{11}$ in pV$^{-1}$) coefficients for Sc$_2$CO$_2$ and (M$'_{2/3}$M$''_{1/3}$)$_2$CO$_2$ (M$'$ = Mo, W; M$''$ = Sc, Y) MXenes [66].

| MXene             | $e_{11}$  | $d_{11}$ |
|-------------------|-----------|-----------|
| Sc$_2$CO$_2$      | 3.333     | 4.137     |
| (Mo$_{2/3}$Sc$_{1/3}$)$_2$CO$_2$ | 44.55     | 29.24     |
| (Mo$_{2/3}$Y$_{1/3}$)$_2$CO$_2$ | 40.33     | 35.91     |
| (W$_{2/3}$Sc$_{1/3}$)$_2$CO$_2$ | 38.82     | 21.67     |
| (W$_{2/3}$Y$_{1/3}$)$_2$CO$_2$ | 35.53     | 24.98     |

5.2. Piezoelectricity

Piezoelectrics are a family of semiconducting materials with an in-plane noncentrosymmetry for which an electrical field can be generated by a mechanical strain because of the shifts of the centers of positive and negative charges. The stress and strain piezoelectric properties of materials under uniaxial strain can be measured by $e_{11}$ and $d_{11}$, respectively. In the MXene family, Sc$_2$CO$_2$ and (M$'_{2/3}$M$''_{1/3}$)$_2$CO$_2$ (M$'$ = Mo, W; M$''$ = Sc, Y) are semiconductors without in-plane centrosymmetry [66]. The piezoelectric coefficients of these materials are summarized in Table 1 [66]. It is found that $d_{11}$ for Sc$_2$CO$_2$ is in the same range of those for well-known transition metal dichalcogenides (MoS$_2$ and MoSe$_2$, 3.65 and 4.55 pV$^{-1}$, respectively) [98]. However, $d_{11}$ for (M$'_{2/3}$M$''_{1/3}$)$_2$CO$_2$ (M$'$ = Mo, W; M$''$ = Sc, Y) is notably larger than those of many piezoelectric 2D materials such as BN, GaAs, GaSe, CaS, and AlSb (in the range of 0.5−3.0 pmV$^{-1}$ [99, 100]) and bulk materials including α-quartz, wurtzite GaN, and wurtzite AlN (2.3, 3.1, and 5.1 pmV$^{-1}$, respectively [101, 102]), which are generally used in industry. This emphasizes
that some semiconducting MXenes may find applications as piezoelectrics.

5.3. Thermoelectricity

Thermoelectric materials, also known as thermoelectrics, are capable of converting temperature differences into useful work. The thermoelectric efficiency is quantified through the dimensionless figure of merit $ZT$, expressed as $S^2\sigma T/K$, where $S$, $\sigma$, $T$, and $K$ are the Seebeck coefficient, electrical conductivity, temperature, and thermal conductivity, respectively. The Seebeck coefficient is a measure of the material's ability to convert temperature differences into electrical energy.

Metallized MXenes, such as Ti$_2$CO$_2$ and W$_2$CO$_2$, have been reported to have reasonable Seebeck coefficients, indicating their potential for thermoelectric applications. However, their electrical conductivities typically remain moderate, which can affect their overall performance.

Metallic MXenes, on the other hand, have demonstrated high electrical conductivities, but their Seebeck coefficients are generally very low. This results in a high power factor $S^2\sigma$, which is a key indicator of a material's thermoelectric performance.

5.4. Superconductivity

Among the MAX phase family, Mo$_2$GaC is a superconductor with a critical temperature ($T_c$) of 4 K. 2D Mo$_2$C MXene has been exfoliated experimentally from a non-MAX-phase structure, Mo$_2$Ga$_x$C$_{1-x}$, and has already been fabricated with various thicknesses through chemical vapor deposition. Other alternatives have been suggested to obtain 2D Mo$_2$C in the literature. It has also been observed experimentally that 2D Mo$_2$C is a superconductor with $T_c < 4$ K. Theoretically, using BCS theory and first-principles calculations, the critical temperature $T_c$ has been predicted for pristine Mo$_2$C and Mo$_2$C functionalized with H, OH, O, S, Se, and Br.

5.5. Catalysis

MXenes are of great interest for their potential as catalysts. The large surface area and high surface reactivity of MXenes make them attractive for various catalytic applications, including water electrolysis. MXenes have been considered for water electrolysis applications in which H$_2$ and O$_2$ molecules are formed through a hydrogen evolution reaction (HER) at the cathode and an oxygen evolution reaction (OER) at the anode. Although Pt is one of the most efficient catalysts for water splitting, its high cost and low availability limit its widespread use.

MXenes are becoming increasingly popular as alternatives to Pt, due to their improved performance and lower cost. For instance, the MXene Ti$_2$CO$_2$ (T = F, OH, O) has been shown to exhibit high activity for the HER. Experimental evidence suggests that Ti- and Mo-based MXenes can be considered as promising candidates for thermoelectric applications.

Further analyses indicate that the thermal conductivities of MXenes are in the range of 10−60 Wm$^{-1}$K$^{-1}$, which is in the same range of those for transition metal dichalcogenides. The values of $ZT$ of Mo$_2$CO$_2$ (M = Ti, Zr, Hf) and Sc$_2$CT$_2$ (T = F, OH, O) have been investigated for temperatures of 300−900 K. The maximum value of $ZT$ for semiconducting MXenes is expected to be less than 1.1.

5.4. Superconductivity

Among members of the MAX phase family, Mo$_2$GaC is a superconductor with a critical temperature ($T_c$) of 4 K. 2D Mo$_2$C MXene has been exfoliated experimentally from a non-MAX-phase structure, Mo$_2$Ga$_x$C$_{1-x}$, and has already been fabricated with various thicknesses through chemical vapor deposition. Other alternatives have been suggested to obtain 2D Mo$_2$C in the literature. It has also been observed experimentally that 2D Mo$_2$C is a superconductor with $T_c < 4$ K. Theoretically, using Bardeen-Cooper-Schrieffer (BCS) theory and DFT electron-phonon interaction calculations, the critical temperature $T_c$ has been predicted for pristine Mo$_2$C and Mo$_2$C functionalized with H, OH, O, S, Se, and Br.

The estimated $T_c$ is in the range from 0 to 13 K and the highest $T_c$ is around 13 K for Mo$_2$C functionalized with H and Br because of their high electron-phonon coupling. The investigation of Fermi surface topology of MAX phases and MXenes with nesting characteristics might be a good strategy to find new superconductors in this family of materials.

5.5. Catalysis

MXenes with a large surface area, high surface hydrophilicity, and surface activities have attracted applications as catalysts and/or catalyst support. One of the widely studied cases, MXenes, have been considered for water electrolysis applications in which H$_2$ and O$_2$ molecules are formed through a hydrogen evolution reaction (HER) at the cathode and an oxygen evolution reaction (OER) at the anode. Although platinum is the most efficient catalysts for water splitting, it has drawbacks due to its high cost and low availability.

MXenes are superior to other 2D catalysts such as MoS$_2$ and CN because of their higher charge transfer abilities. It has been shown that O-terminated MXenes such as Ti$_3$CO$_2$ and W$_2$CO$_2$ possess Gibbs free energies close to 0 eV for hydrogen adsorption, suitable for HER. Experimental evidence of the HER activity of Ti- and Mo-based MXenes suggests that Mo$_2$CT$_x$
and Ti$_3$C$_2$T$_x$ exhibit a good HER activity for generating hydrogen from water and ammonia borane, respectively [117, 118]. A detailed theoretical investigation, e.g., shown in Fig. 14, indicates that among all MXenes, Mo$_2$CT$_x$ possesses the most promising surface activity for the HER [119]. The catalytic properties of MXenes can be improved by the introduction of metal atoms such as Fe. This is because less electronegative elements such as Fe can transfer more charge to the O atom of water; hence, the O–H bonds of water are weakened, leading to a better HER activity. Furthermore, the hybrid structure of Ti$_3$C$_2$/g-C$_3$N$_4$ improves the performance for the OER as compared to the case of the pristine MXene because the charge transfer between Ti atoms and graphitic carbon nitride facilitates the electron transfer for O$_2$ evolution [120, 121]. Another study has shown that Mo$_2$CT$_x$ surfaces can be suitable substrates for Pd atom anchoring to produce O$_2$ from CO molecules [122].

5.6. Photocatalysis

Some MXenes are semiconducting with light absorption in the visible light region and good catalytic properties. Hence, they have potential applications for various photocatalytic reactions. The production of hydrogen by water splitting on semiconductor substrates via sunlight is an example of such photocatalytic reactions. This process involves electron-hole pair generation by absorbing solar light in the photocatalytic material. Material with photocatalytic properties possesses a band gap larger than 1.23 eV for the absorption visible light and has redox potentials located between the valence and conduction band edges [123]. Owing to semiconducting characteristics, Ti$_3$CO$_2$, Zr$_2$CO$_2$, Hf$_2$CO$_2$, Sc$_2$CO$_2$, and Sc$_2$CF$_2$ are candidates for photocatalytic applications. As shown in Fig. 15(a), Ti$_3$CO$_2$, Sc$_2$CO$_2$, and Sc$_2$CF$_2$ are not suitable for water splitting because the water redox potentials are beyond the band edges. Considering the optical properties of the remaining candidates, Zr$_2$CO$_2$ and Hf$_2$CO$_2$, their absorption peaks are located in the visible light energy window [see Fig. 15(a)]. Therefore, they can be used for the HER via a photocatalytic reaction with water [123].

Further studies indicate that heterostructures of metallic MXenes (e.g., Ti$_3$C$_2$) with other semiconductors (e.g., TiO$_2$) can be used for various photocatalytic reactions. For example, the photocatalytic activity of Ti$_3$C$_2$T$_x$ sharply increases with TiO$_2$; an improvement of 400% is observed for the HER [124]. In another report, TiO$_2$ nanoplates grown on Ti$_3$C$_2$ shows improved photocatalytic performance, 2.8 times higher than that of pure TiO$_2$ for CO$_2$ reduction. This increase in the production can be attributed to the position of the TiO$_2$ conduction band edges, which is more negative than the Fermi energy of the MXene; hence, electrons are transferred to Ti$_3$C$_2$ with a smaller energy barrier. Therefore, an electron–hole pair can be easily separated without recombination [125]. A recent experiment on a Ti-based MXene has successfully prepared CdS/Ti$_3$C$_2$ heterostructure and observed an improvement in the photocatalytic activity. The photocatalytic activity of CdS is low (105 µmol h$^{-1}$ g$^{-1}$), which varies linearly with the amount of Ti$_3$C$_2$, reaching to a very high activity of 14322 µmol h$^{-1}$ g$^{-1}$ for the HER. This improvement can again be correlated with the electron transfer from CdS to the MXene, which pushes the conduction band edge to align with the standard hydrogen electrode (SHE). The versatility of Ti-MXene was verified by fabricating ZnS and Zn doped CdS with Ti$_3$C$_2$ nanoparticles [126].

5.7. Ion batteries

Owing to their excellent electrical conductivity, large surface areas, and environmentally friendly behavior, MXenes have much-attracted attention for applications in energy storage such as capacitors and alkali and metal batteries [54, 127, 128]. It was found that Ti$_3$C$_2$ monolayers can have a capacity (Li-ion) of 320 mAh g$^{-1}$. Surface functionalization with OH and F groups resulted in the decrease in the specific capacity to 130
and 67 mAh g\(^{-1}\), respectively, considering the increase in the atomic weight. The calculated diffusion barrier along the minimum energy pathway for a Li atom on a bare Ti\(_2\)C\(_2\) sheet is 0.005 eV. The introduction of OH and F groups leads to the increase in the diffusion barrier to 0.36 and 1.02 eV, respectively [129]. It has also been observed that the formation of additional Li layers on lithiated O-terminated Ti\(_2\)C\(_2\) accounts for the higher gravimetric capacity observed in a delaminated Ti\(_2\)CO\(_2\) colloidal solution intercalated with dimethyl sulphoxide [130]. It has also been predicted that the coverage of alkali ions on Ti\(_2\)C\(_2\) and the adsorption energy are related to their effective ionic radii. The increase in the effective ionic radius of an alkali increases the interaction energy while it decreases the coverage [131].

The calculations for Ti\(_2\)C, its functionalized monolayers, and its defective layers indicate that the presence of vacancies affects the diffusion behavior and changes the barrier of lithium atoms [132]. A systematic analysis of various 2D MXenes finds that Ti\(_2\)C has a low diffusion barrier for Li in both the pristine and defective state. Li-atom diffusion has a relatively higher energy barrier on a Ti\(_2\)CX\(_2\) (X = O, OH) graphene heterostructure as compared to the Ti\(_2\)CX\(_2\) monolayer and is lower than graphite by 0.5 eV [133]. On the other hand, the open-circuit voltage of Ti\(_2\)CO\(_2\)/graphene is enhanced to 1.49 V, while sulfur-terminated Ti\(_2\)C shows a relatively low energy barrier for Li atoms and has the highest affinity for polysulfides [134]. Moreover, the lithium-sulfur storage capacity of Ti-based MXenes was explored recently, and it was found that OH groups can entrap the Li\(_2\)S\(_8\) chains formed on top of them MXene [135].

The success achieved in the case of Li-ion batteries has stimulated research on utilizing MXenes for other alkali and alkali-earth metal batteries. Accordingly, the adsorption of metal ions such as monovalent (Na and K) and multivalent (Mg, Ca, and Al) ions on layered Ti\(_2\)CX\(_2\) (X = O, F, OH) has been studied [136]. A bare MXene has higher capacities and greater mobilities for metal ions. Na and K ions were found to intercalate more efficiently as compared to other metal ions. Furthermore, O-terminated MXenes decompose into bare MXenes during Mg, Ca, and Al ions intercalation. Monovalent metal ions Na and K have a low diffusion barrier on the Ti\(_2\)CO\(_2\) monolayer as compared to the multivalent metal ions Mg, Ca, and Al. With a low diffusion barrier for Na on Ti\(_2\)C\(_2\) and its functionalized MXenes, a further increase in the interlayer separation lowers the redox potential. Furthermore, the volume change was observed during sodation and desodation on pristine and F- and O-functionalized Ti-based MXenes, which are favorable for the cycling performance [137].

With the aim of increasing the electron density, which eventually decreases the diffusion barriers of electron-rich species, nitrogen-containing MXenes have been studied. Li adsorption and diffusion on trimetallic Ti\(_3\)CN and its F-, O-, and OH-functionalized MXenes were studied [138]. Li atoms preferentially adsorb on the nitrogen side in Ti\(_3\)CN. In the functionalized materials, Li atoms tend to be adsorbed on the carbon side. The diffusion barriers are in the range of 0.2–0.3 eV for functionalized Ti\(_3\)CN. The potential use of Ti\(_2\)N and its functionalized derivatives for use as anode materials was recently tested [139]. The adsorption energies of cations including Li, Na, K, Mg, Ca, and Al and the open-circuit voltage suggest that Ti\(_2\)N monolayers are a promising candidate for the anode material in rechargeable batteries. An electron localization function analysis of carbide and nitride MXenes suggests that the N atom in Ti\(_2\)N needs one less electron from Ti to form an ionic bond, thereby creating a non-bonding electron cloud on the Ti\(_2\)N surface. The presence of negative electron cloud results in a low diffu-
Figure 18: Snapshots of molecular dynamics for hydrogen adsorption on Ti$_2$C at 300 and 400 K after 1.5 ps viewed from top and side of Ti$_2$C. Physisorbed and adsorbed H$_2$ by Kubas interactions are indicated by the cyan and red spheres, respectively [153].

The high adsorption strength and higher charge transfer towards Sc$_2$CO$_2$. By applying tensile strains or external electric fields, the adsorption strength of SO$_2$ can be controlled, and even the reversible release of captured SO$_2$ can be achieved [152].

5.9. Hydrogen storage

MXenes have also been investigated for possible hydrogen storage. For example, it was predicted that hydrogen molecules on the surfaces of Ti$_2$C are adsorbed in molecular form and then dissociated to form hydrides, while hydrogen molecules in the second and third layers from the surfaces are adsorbed in molecular form [153]. The hydrides constitute 1.7 wt%, and molecular hydrogen has a reversible capacity of 3.4 wt%. Molecular dynamics studies show that the hydrogen that exists with a Kubas-type interaction departs, leaving the hydrides intact on the surface (see Fig. 18). This clearly justifies the reversible uptake of hydrogen on the Ti$_2$C layer. A similar conclusion has been reached for Sc$_2$C and V$_2$C [153, 154]. A recent study has shown that the hydrogen storage capacity of Cr$_2$C can reach 7.6 wt%, where 1.2 wt% is due to chemisorption, 3.2 wt% is due to the Kubas interaction, and 3.2 wt% exists in molecular form with a weak electrostatic interaction for hydrogen storage [155]. Hence, a reversible hydrogen storage capacity of 6.4 wt% can be achieved with a binding energy 0.1–0.44 eV/H$_2$ on the Cr$_2$C surface [155].

6. Conclusions and outlook

MXenes with rich physics and chemistry, as well as deep structural and compositional diversities, offer a fertile ground for performing fundamental and multidisciplinary research. Nevertheless, until now the synthesis of MXenes with a uniform and pure surface termination is an experimental challenge, and it is an obstacle in realizing the full potential of proposed many electronic-based phenomena and applications. Therefore, it is valuable to investigate the mixed functionalization of MXene to explore its applications that are not significantly affected by surface termination. The mixed functionalization can also lead to the formation of various interfaces, such as sharp and diffusive interfaces, at
the surface of MXenes. Experimental attempts should be made to isolate the pristine MXenes for their full characterization and subsequently controlled functionalization as well.

Different types of magnetic orders with the large SOC in MXenes promise novel quantum anomalous Hall systems. The response to the external electric field, mechanical strain, and photo-irradiation are the key to tailoring the novel phenomena and applications of MXene-based devices. Exploring the effect of the gate voltage on controlling the magnetic orders in MXenes is an exciting area of science. Moreover, very little has been explored about the superconductivity in MXenes. In this regard, the theoretical investigation of the Fermi surface nesting and electron-phonon couplings in various MAX phases and MXenes are crucial.

Most probably, vertical and lateral heterostructures of MXene with other 2D materials will be synthesized in the near future. The effect of van der Waals interactions on stability and electronic properties of multilayered MXenes should be investigated. The interfacial physics of such junctions will be of fundamental interest for device applications. Furthermore, the effect of electric field on monolayers have already been investigated. This should be extended to few layers, multilayers, and heterostructures of MXenes to examine the electron or hole accumulation on the surface and interface and their influence on electronic properties. The effect of electron/hole injection on chemical bonding and elastic properties of MXene should be investigated for making artificial muscles and various actuator applications. The electron-hole coupling of the heterostructure of MXenes should be examined for solar cell applications. The electronic properties of MXenes in the presence of the magnetic field and the absorption/reflection of the magnetic field are vital for understanding shielding effect.

The development of classical potentials or phase field parameters for performing large-scale molecular dynamics simulation is necessary to study the biological and composite applications of MXenes, to simulate the chemical exfoliation of MAX phases using different etchant solutions, to understand the mechanism of hydration of different charged alkali metals between MXene layers and its effects on interlayer distances, and to study the hydrophilicity of MXene surfaces. The effects of using a mixture of A elements in synthesis and exfoliation of MAX phases should be addressed computationally. It is also interesting to investigate the mechanical exfoliation of MAX phases both theoretically and experimentally in detail and compare the resulting structures with those obtained from chemical exfoliations.

It is highly desirable to study the thermal conductivity of MXenes and screen out the promising thermoelectric candidates. The estimation of relaxation time is essential to evaluate the electrical conductivity and figure of merits of MXenes and MAX phases. The effect of compression on thermoelectric properties of MXenes is of fundamental interest. The investigation of electron transport and optical conductivity of MXenes is essential for electronic device applications. It is also worth determining which of MXenes can be good candidates for cathode or anode electrode applications. Developing new in- and out-of-plane ordered double transition metals MXenes is also important for assessing various magnetic orders. The physics behind the excellent piezoelectricity of the in-plane ordered double transition metals should also be investigated. The possible Rashba effect in janus MXenes needs to be examined in more details.

The effects of M and/or X vacancies in MXenes should be explored on various applications such as ion batteries and electrode structural flexibility. The potential applications of vacancy-ordered in-plane MXenes for gas storage should also be studied. Detailed and systematic analyses are required on nanoribbons, nanoscrolls, clusters, or quantum dots of MXenes. Finally, it is of great interest to synthesize the multifunctional group III based MXenes (e.g., Sc2CO2), which, due to their surface polarization, might be good candidates for polarization-driven catalysis.

Acknowledgments

M.K. is grateful to RIKEN Advanced Center for Computing and Communication (RCCC) for the allocation of the computational resources of the RIKEN supercomputer system (HOKUSAI GreatWave). Some of the calculations were also performed on the Numerical Materials Simulator at NIMS. M.K. gratefully acknowledges the support by a Grant-in-Aid for Scientific Research (No. 17K14804) from MEXT Japan. A.M. and A.K.S. acknowledge the computation facilities at the Materials Research Centre, the Thematic Unit of Excellence, and the Supercomputer Education and Research, Indian Institute of Science, Bangalore, India. A.K.S. and A.M. are thankful for support from DST Nano Mission, and A.M. acknowledges UGC India for a Senior Research Fellowship.
References

[1] K. S. Novoselov, A. Mishchenko, A. Carvalho, A. H. Castro Neto, 2D materials and van der Waals heterostructures, Science 353 (2016) 9439.

[2] M. Naguib, M. Kurtoglu, V. Presser, J. Lu, J. Niu, M. Heon, L. Hultman, Y. Gogotsi, M. W. Barsoum, Two-dimensional nanocrystals produced by exfoliation of Ti3AlC2. Adv. Mater. 23 (2011) 4248–4253.

[3] M. Naguib, O. Mashatlar, J. Carle, V. Presser, J. Lu, L. Hultman, Y. Gogotsi, M. W. Barsoum, Two-dimensional transition metal carbides, ACS Nano 6 (2012) 1322–1331.

[4] M. W. Barsoum, The M_{X_{1-x}A_x} phases: A new class of solids: Thermodynamically stable nanolaminates, Prog. Solid State Chem. 28 (2000) 201–281.

[5] M. A. Hope, A. C. Forse, K. J. Griffith, M. R. Lukatskaya, M. Ghidiru, Y. Gogotsi, C. P. Grey, NMR reveals the surface functionalisation of Ti3C2 MXene, Phys. Chem. Chem. Phys. 18 (2016) 5099.

[6] J. Halim, K. M. Cook, M. Naguib, P. Eklund, Y. Gogotsi, J. Rosen, and M. W. Barsoum, X-ray photoelectron spectroscopy of select multi-layered transition metal carbides (MXenes). Appl. Surf. Sci. 362 (2016) 406–417.

[7] M. Ghidiru, M. R. Lukatskaya, M. Q. Zhao, Y. Gogotsi, and M. W. Barsoum, Conductive two-dimensional titanium carbide ‘clay’ with high volumetric capacitance, Nature 516 (2014) 78–81.

[8] J. Halim, M. R. Lukatskaya, K. M. Cook, J. Lu, C. R. Smith, L.-Åke Näslund, S. J. May, L. Hultman, Y. Gogotsi, P. Eklund, and M. W. Barsoum, Transparent conductive two-dimensional titanium carbide epitaxial thin films, Chem. Mater. 26 (2014) 2374–2381.

[9] M. W. Barsoum, M. Radovic, Elastic and Mechanical Properties of the MAX Phases, Annu. Rev. Mater. Res. 41 (2011) 195–227.

[10] M. Khazaei, M. Arai, T. Sasaki, M. Estili, Y. Sakka, Trends in electronic properties and structural properties of MAX phases: a first-principles study on M2AlC (M = Sc, Ti, Cr, Zr, Nb, Mo, Hf, or Ta), M2AlN, and hypothetical M2AlB phases J. Phys.: Condens. Matter 26 (2014) 505503.

[11] M. Khazaei, A. Ranjbar, M. Arai, T. Sasaki, S. Yunoki, Electronic properties and applications of MXenes: a theoretical review, J. Mater. Chem. C 5 (2017) 2488–2503.

[12] N. M. Caffrey, Effect of mixed surface terminations on the structural and electrochemical properties of MAX phases: a first-principles study on M2AlC and M2AlN. Phys. Chem. Chem. Phys. 12 (2010) 13520–13530.

[13] T. Hu, M. Hu, B. Gao, W. Li, X. Wang, Screening surface structure of MXenes by high-throughput computation and vibrational spectroscopic confirmation, J. Phys. Chem. C 122 (2018) 18501–18509.

[14] P. Persson, L.-Å. Näslund, J. Halim, M. W. Barsoum, V. Darakchieva, J. Pálásiaitė, J. Rosen, P. O. ÅPersson, On the organization and thermal behavior of functional groups on Ti3C2 MXene surfaces in vacuum, 2D Mater. 5 (2018) 015002.

[15] B. Anasori, M. R. Lukatskaya, Y. Gogotsi, 2D metal carbides and nitrides (MXenes) for energy storage, Nat. Rev. 2 (2017) 16098.

[16] B.-M. Jun, S. Kim, J. Heo, C. M. Park, N. Hef, M. Jang, Y. Huang, J. Han, Y. Yoon, Review of MXenes as new nanomaterials for energy storage/delivery, and selected environmental applications. Nano Res. (2018) https://doi.org/10.1007/s12274-018-2225-3.

[17] J. Pang, R. G. Mendes, A. Bachmatiuk, L. Zhao, H. Q. Ta, T. Gemming, H. Liu, Z. Liu, Mark H. Rummeli, Applications of 2D MXenes in energy conversion and storage systems, Chem. Rev. Soc. 48 (2019) 72–133.

[18] A. L. Ivanovskaia and A. N. Enyashin, Graphene-like transition-metal nanocaricides and nanonitrides. Russ. Chem. Rev. 82 (2013) 735–746.

[19] N. K. Chaudhuri, H. Jin, B. Kim, D. S. Baek, S. H. Joo, K. Lee, MXene: an emerging two-dimensional material for future energy conversion and storage applications, J. Mater. Chem. A 5 (2017) 24564–24579.

[20] J. Zhu, E. Ha, G. Zhao, Y. Zhou, D. Huang, G. Yue, L. Hu, N. Sun, Y. Wang, L. Y. S. Lee, C. Xu, K.-Y. Wong, D. Astruc, and P. Zhao, Recent advance in MXenes: A promising 2D material for catalysis, sensor and chemical adsorption, Coord. Chem. Rev. 352 (2017) 306–327.

[21] H. Wang, Y. Wu, X. Yuan, G. Zeng, J. Zhou, X. Wang, J. W. Chew, Clay-inspired MXene-based electrochemical devices and photo-electrocatalyst: state-of-the-art progresses and challenges, Adv. Mater. 30 (2018) 1704561.

[22] X. Li, C. Wang, Y. Cao, G. Wang, Functional MXene materials: progress of their applications, Chem. Asian J. 13 (2018) 2742–2757.

[23] X. Zhang, Z. Zhang, Z. Zhou, MXene-based materials for electrochemical energy storage, J. Energy Chem. 27 (2018) 73–85.

[24] Y. Zhang, L. Wang, N. Zhang, Z. Zhou, Adsorptive environmental applications of MXene nanomaterials: a review, RSC Adv. 8 (2018) 19895–19905.

[25] K. Hantanarisirakul and Y. Gogotsi, Electronic and optical properties of 2D transition metal carbides and nitrides (MXenes) Adv. Mater. (2018), 1804779.

[26] H. Lin, Y. Chen, and J. Shi, Insights into 2D MXenes for versatile biomedical applications: current advances and challenges ahead, Adv. Sci. 5 (2018) 1800518.

[27] M. Naguib, J. Halim, J. Lu, K. M. Cook, L. Hultman, Y. Gogotsi, M. W. Barsoum, New Two-dimensional niobium and vanadium carbides as promising materials for Li-Ion batteries, J. Am. Chem. Soc. 135 (2013) 15966–15969.

[28] M. Ghidiru, M. Naguib, C. Shi, O. Mashtalir, L. M. Pan, B. Zhang, J. Yang, Y. Gogotsi, S. J. L. Billinge, M. W. Barsoum, Synthesis and characterization of two-dimensional Nb2C3 (MXene), Chem. Commun. 50 (2014) 9517–9520.

[29] J. Zhou, X. Zha, F. Y. Chen, Q. Ye, P. Eklund, S. Du, Q. Huang, A two-dimensional zirconium carbide by selective etching of Al2C3 from nanolaminated Zr2AlC3 Angew. Chem.-Int. Edit. 55 (2016) 5008–5013.

[30] P. Urbankowski, B. Anasori, T. Makaryan, D. Er, S. Kota, P. L. Walsh, M. Zhao, V. B. Shenoy, M. W. Barsoum, Y. Gogotsi, Synthesis of two-dimensional titanium nitride Ti3N4 (MXene), Nanoscale 8 (2016) 11385–11391.

[31] B. Soundiraraju, B. K. George, Two-dimensional titanium nitride (Ti3N4) MXene: synthesis, characterization, and potential application as surface-enhanced Raman scattering substrate, ACS Nano 11 (2017) 8892–8900.

[32] M. Alhabeb, K. Maleski, T. S. Mathis, A. Sarycheva, C. B. Hater, S. Uzun, A. Levitt, and Y. Gogotsi, Selective etching of silicon from Ti3SiC2 (MAX) To Obtain 2D Titanium Carbide (MXene), Angew. Chem. Int. Ed. Engl. 57 (2018) 5444–5448.

[33] M. H. Tran, T. Schäfer, A. Shahreraei, M. Dürchschnabel, L. Molina-Luna, U. I. Kramm, C. S. Birkel, Adding a new member to the MXene family: Synthesis, structure, and electrocatalytic activity for the hydrogen evolution reaction of V2C3Ti3, ACS Appl. Energy Mater. 1 (2018) 3908–3914.

[34] J. Yang, M. Naguib, M. Ghidiru, L.-M. Pan, J. Gu, J. Nanda, J. Halim, Y. Gogotsi, M. W. Barsoum, Two-dimensional Nb-based
M. Dahlqvist, A. Petruhins, J. Lu, B. C. Hosler, Experimental and theoretical characterization of ordered MAX phases Mo$_2$TiAlC$_2$ and Mo$_2$Ti$_3$AlC$_2$, J. Appl. Phys. 118 (2015) 94304.

R. Meshkian, Q. Tao, M. Dahlqvist, J. Lu, L. Hultman and J. Rosen, Theoretical stability and materials synthesis of a chemically ordered MAX phase, Mo$_2$Sc$_{13}$C$_2$, and its two-dimensional derivative Mo$_2$Sc$_2$MXene, Acta Mater. 125 (2017) 476–480.

M. Dahlqvist, J. Lu, S. Kota, R. Meshkian, J. Halim, J. Palisaitis, L. Hultman, M. W. Barsoum, P. O. Persson, J. Rosen, Two-dimensional Mo$_3$Sc$_3$MXene with divacancy ordering prepared from parent 3D laminate with in-plane chemical ordering, Nat. Commun. 8 (2017) 14949.

R. Meshkian, M. Dahlqvist, J. Lu, B. Wickman, J. Halim, J. Thörnberg, Q. Tao, S. Li, S. Intikhab, J. Snyder, M. W. Barsoum, M. Yildizhan, J. Palisaitis, L. Hultman, P. O. Persson, J. Rosen, W-based atomic laminates and their 2D derivative W$_{133}$C MXene with vacancy ordering, Adv. Mater. 30 (2018) 1706409.

L. Chen, Martin Dahlqvist, T. Lapauw, B. Tunca, F. Wang, J. Lu, R. Meshkian, K. Lambrinou, B. Blanpain, J. Vleugels, J. Rosen Inorg. Chem. 57 (2018) 6237–6249.

M. Dahlqvist, A. Petruhins, J. Lu, L. Hultman, J. Rosen, Theoretical and experimental exploration of a novel in-plane chemically-ordered, (Cr$_6$)$_2$M$_{133}$TiC$_2$-MAX Phase with MoSc and Y. Cryst. Growth Des. 17 (2017) 5704–5711.

R. Meshkian, M. Dahlqvist, J. Lu, B. Wickman, J. Halim, J. Thörnberg, Q. Tao, S. Li, S. Intikhab, J. Snyder, M. W. Barsoum, M. Yildizhan, J. Palisaitis, L. Hultman, P. O. Persson, J. Rosen, W-based atomic laminates and their 2D derivative W$_{133}$C MXene with vacancy ordering, Adv. Mater. 30 (2018) 1706409.

P. Srivastava, A. Mishra, H. Mizuseki, K. R. Lee, A. K. Singh, Mechanistic insight into the chemical exfoliation and functionalization of Ti$_x$C$_2$ MXene, ACS Appl. Mater. Interfaces 10 (2018) 24255–24264.

M. Khazaei, A. Ranjbar, K. Esfarjani, D. Bogdanovski, R. Dronskowski, S. Yunoki, Insights into exfoliation possibility of MAX phases to MXenes, Phys. Chem. Chem. Phys. 20 (2018) 8579–8592.

Z. Guo, L. Zhu, J. Zhou, Z. Sun, Microscopic origin of MXenes derived from layered MAX phases, RSC Adv. 5 (2015) 25403–25408.

M. Khazaei, M. Arai, T. Sasaki, M. Estili, Y. Sakka, The effect of the interlayer element on the exfoliation of layered Mo$_2$AC (A = Al, Si, P, Ga, Ge, As or In) MAX phases into two-dimensional Mo$_2$AC MXenes, Sci. Tech. Adv. Mater. 15 (2014) 014208.

M. Yi, Z. Shen, A review on mechanical exfoliation for the scalable production of graphene, J. Mater. Chem. A 3 (2015) 11700.
gap predictions of functionalized MXene, Chem. Mat. 30 (2018) 4031–4038.

[69] X.-F. Yu, Jian-B. Cheng, Z.-B. Liu, Q.-Z. Li, W.-Z. Li, X. Yang, and B. Xiao, The band gap modulation of monolayer Ti$_2$CO$_2$ by strain, RSC Adv. 5 (2015) 30438.

[70] Y. Lee, Y. Hwang, S. Cho, and Y.-C. Chung, Achieving a direct band gap in oxygen functionalized monolayer scandium carbide by applying an electric field, Phys. Chem. Chem. Phys. 16 (2014) 26273.

[71] Y. Lee, Y. Hwang, and Y.-C. Chung Achieving type I, II, and III heterojunctions using functionalized MXene, ACS Appl. Mater. Interfaces 7 (2015) 7163–7169.

[72] A. S. Ingason, M. Dahlehqvist, J. Rosen, Magnetic MAX phases from theory and experiments; a review, J. Phys.: Condens. Matter 28 (2016) 433003.

[73] G. Gao, G. Ding, J. Li, K. Yao, M. Wu, M. Qian, Monolayer MXenes: promising half-metals and spin gapless semiconductors, Nanoscale 8 (2016) 8986–8991.

[74] C. Si, J. Zhou, Z. Sun, Half-metallic ferromagnetism and surface functionalization-induced metal-insulator transition in graphene-like two-dimensional Cr$_2$C$_2$ crystals, ACS Appl. Mater. Interfaces 7 (2015) 17510–17515.

[75] J. He, P. Lyu, L. Z. Sun, Á. M. García, P. Nachtigall, High temperature spin-polarized semiconductivity with zero magnetization in two-dimensional Janus MXenes, J. Mater. Chem. C 4 (2016) 6500–6509.

[76] H. Kumar, N. C. Frey, L. Dong, B. Anasori, Y. Gogotsi, V. B. Shenoy, Tunable Magnetism and Transport Properties in Nitride MXenes, ACS Nano 11 (2017) 7648–7655.

[77] L. Dong, H. Kumar, B. Anasori, Y. Gogotsi, V. B. Shenoy, Rational design of two-dimensional metallic and semiconducting spintronic materials based on ordered double-transition-metal MXenes, J. Phys. Chem. Lett. 8 (2017) 422–428.

[78] W. Chen, H.-F. Li, X. Shi, H. Pan, Tension-tailored electronic and magnetic switching of 2D Ti$_2$NO$_2$, J. Phys. Chem. C 121 (2017) 25729–25735.

[79] S.-S. Li, S.-J. Hu, W.-X. Ji, P. Li, K. Zhang, C.-W. Zhang, and S.-S. Yan, Emergence of ferromagnetic half-metallicity in two-dimensional MXene Mo$_2$N$_2$F$_2$, Appl. Phys. Lett. 111 (2017) 202405.

[80] N. C. Frey, H. Kumar, B. Anasori, Y. Gogotsi, V. B. Shenoy, Tuning noncollinear spin structure and anisotropy in ferromagnetic nitrugel MXenes, ACS Nano 12 (2018) 6319–6325.

[81] W. Sun, Y. Xie, and P. R. C. Kent, Double transition metal MXenes with wide band gaps and novel magnetic properties, Nano Lett. 11 (2019) 356–364.

[82] J. He, G. Ding, C. Zhong, S. Li, D. Li, and G. Zhang, Nanoscale 11 (2019) 202405.

[83] J.-J. Zhang, L. Lin, Y. Zhang, M. Wu, B. I. Yakobson, and S. Dong, Type-II Multiferroic Hf$_2$VC$_2$F$_2$ MXene monolayer with high transition temperature, J. Am. Chem. Soc. 140 (2018) 9768–9773.

[84] P. Ravendran, A. Delin, B. Johansson, O. Eriksson, J. M. Wills, Electronic structure, chemical bonding, and optical properties of ferroelectric and antiferroelectric NaNO$_2$, Phys. Rev. B 59 (1999) 1776–1786.

[85] G. R. Berdiyorov, Optical properties of functionalized Ti$_2$C$_2$T$_2$ (T= F, O, OH) MXene: First-principles calculations, AIP Adv. 6 (2016) 055105.

[86] Y. Bai, K. Zhou, N. Srikanth, J. H. L. Pang, X. He, R. Wang, Dependence of elastic and optical properties on surface terminated groups in two-dimensional MXene monolayers: a first-principles study, RSC Adv. 6 (2016) 35731–35739.

[87] H. Zhang, G. Yang, X. Zuo, H. Tang, Q. Yang, G. Li, Computational studies on the structural, electronic and optical properties of graphene-like MXenes (M$_2$CT$_3$: M= Ti, Zr, Hf; T= O, F, OH) and their potential applications as visible-light driven photocatalysts, J. Mater. Chem. A 4 (2016) 12913–12920.

[88] Y. Guo, Y. Sun, B. Liu, Q. Zhang, Q. Peng, Two-dimensional scandium-based carbides (MXene): Band gap modulation and optical properties, J. Alloys Compd. 712 (2017) 752–759.

[89] A. Chandrasekaran, A. Mishra, A. K. Singh, Ferroelectricity, antiferroelectricity, and ultrathin 2D electron/hole gas in multifunctional monolayer MXene, Nano Lett. 17 (2017) 3290–3296.

[90] G. Ying, S. Kota, A. D. Dillon, A. T. Farafman, M. W. Barsoum, Conductive transparent V$_2$CT$_4$ (MXene) films, FlatChem 8 (2018) 25.

[91] R. Li, L. Zhang, L. Shi, and P. Wang, MXene Ti$_2$C$_2$: an effective 2D light-to-heat conversion material, ACS Nano 11 (2017) 3752–3759.

[92] Khazaei, M. Arai, M. Sasaki, T. Ranjarb, A. Liang, Y. Yunoki, S. OH-terminated two-dimensional transition metal carbides and nitrides as ultralow work function materials, Phys. Rev. B 92 (2015) 075411.

[93] Y. Liu, H. Xiao, W. A. Goddard III, Schottky-barrier-free contacts with two-dimensional semiconductors by surface-engineered MXenes, J. Am. Chem. Soc. 138 (2016) 15853–15856.

[94] M. Khazaei, M. Ranjarb, M. Ghorbani-Asl, M. Arai, T. Sasaki, Y. Liang, S. Yunoki, Nearly free electron states in MXenes, Phys. Rev. B 93 (2016) 205125.

[95] Q. Peng, J. Guo, Q. Zhang, J. Xiang, B. Liu, A. Zhou, R. Liu, Y. Tian, Unique lead adsorption behavior of activated hydroxyl group in two-dimensional titanium carbide, J. Am. Chem. Soc. 136 (2014) 4113–4116.

[96] N. Aildoust, G. Bian, S.-Y. Xu, R. Sarkar, M. Neupane, C. Liu, I. Belopoliski, D.-X. Qu, J. D. Denlinger, F.-C. Chou and M. Z. Hasan, Observation of monolayer valence band spin-orbit effect and induced quantum well states in Mo$_2$X$_2$, Nat. Commu. 5 (2014) 4673.

[97] M. Otani and S. Okada, Field-induced free-electron carriers in graphite, J. Phys. Soc. Jpn 79 (2010) 073701.

[98] M. N. Bloshsky, H. L. Zhuang, A. K. Singh, R. G. Hennig, Ab initio prediction of piezoelectricity in two-dimensional materials, ACS Nano 9 (2015) 9865–9869.

[99] W. Li, J. Li, Piezoelectricity in two-dimensional group-III monochalcogenides, Nano Res. 8 (2015) 3796–3802.

[100] C. Sekvi, D. Čakir, O. Gülsen, F. M. Peeters, Peculiar piezoelectric properties of soft two-dimensional materials, J. Phys. Chem. C 120 (2016) 11948–11953.

[101] R. Behmann, Elastic and piezoelectric constants of alpha-quartz, Phys. Rev. 110 (1958) 1060–1061.

[102] C. M. Lueng, H. L. W. Chan, C. Surya, C. L. Choy, Piezoelectric coefficient of aluminum nitride and gallium nitride, J. Appl. Phys. 88 (2000) 5360–5363.

[103] S. Kumar and U. Schwingschlägl, Thermolectric performance of functionalized Sc$_2$C MXenes, Phys. Rev. B 94 (2016) 035405.

[104] A. N. Gandhi, H. N. Alshareef, U. Schwingschlägl, Thermo-electric performance of the MXenes Mo$_2$CO$_2$: an e-value driven study, RSC Adv. 6 (2016) 25734–25739.

[105] S. Sarikurt, D. Čakir, M. Keçeli, C. Sekvi, The influence of surface functionalization on thermal transport and thermoelectric properties of MXene monolayers, Nanoscale 10 (2018) 8859–8868.

[106] W. Jeitschko, H. Nowotny, F. Benesovsky, Kohlenstoffhülle: Verbindungen (H-Phase), Monatsh. Chem. 94 (1963) 672–676.

[107] R. Meshkian, L. ÂNslund, J. Hålim, J. Lu, M. W. Bar-
J. Rosén, Synthesis of two-dimensional molybdenum carbide, Mo$_2$C, from the gallium based atomic laminate Mo$_2$Ga$_3$C, Scripta Mater. 108 (2015) 147–150.

[108] C. Xu, L. Wang, Z. Liu, L. Chen, J. Guo, N. Kang, X.-L. Ma, H.-M. Cheng, W. Ren, Large-area high-quality 2D ultrathin Mo$_2$C superconducting crystals, Nat. Mater. 14 (2015) 1135–1141.

[109] D. Geng, X. Zhao, Z. Chen, W. Sun, W. Fu, J. Chen, W. Liu, W. Zhou, K. P. Loh, Direct synthesis of large-area 2D Mo$_2$C on in situ grown graphene, Adv. Mater. 29 (2017) 1700072.

[110] W. Sun, Y. Li, B. Wang, X. Jiang, M. I. Katsnelson, P. Korzhavyi, O. Eriksson, and I. D. Marco, A new 2D monolayer Bi$_2$Xene, M$_2$(Mo=Te,Os), Nanoscale 8 (2016) 15753.

[111] J. Bardeen, L. N. Cooper, J. R. Schrieffer, Theory of superconductivity, Phys. Rev. 108 (1957) 1175–1204.

[112] J. Lei, A. Kutana, B. I. Yakobson, Predicting stable phase monolayer Mo$_2$C (MXene), a superconductor with chemically-tunable critical temperature, J. Mater. Chem. C 5 (2017) 3438–3444.

[113] J.-J. Zhang, S. Dong, Superconductivity of monolayer Mo$_2$C: the key role of functional groups, J. Chem. Phys. 146 (2017) 034705.

[114] Y.-D. Fu, B. Wang, Y. Teng, X.-S. Zhu, X.-X. Feng, M.-F. Yan, P. Korzhavyi, and W. Sun, The role of group III E elements in Nb$_n$AC$_3$ MAX phases (A = Al, Si, Ga, Ge) and the unusual anisotropic behavior of the electronic and optical properties, Phys. Chem. Chem. Phys. 19 (2017) 15471–15483.

[115] C. Ling, L. Shi, Y. Ouyang, J. Wang, Searching for highly active catalysts for hydrogen evolution reaction based on O-terminated MXenes through a simple descriptor, Chem. Mat. 28 (2016) 9026–9032.

[116] G. Gao, A. P. O’Mullane, A. Du, 2D MXenes: A new family of promising catalysts for the hydrogen evolution reaction, ACS Catal. 7 (2016) 494–500.

[117] N. K. Chaudhari, H. Jin, B. Kim, and D. S. Baek, S. H. Joo, K. Heon, M. W. Barsoum, Y. Gogotsi, Interfacial engineering of layered carbides and carbonitrides, Nature commun. 4 (2013) 1716.

[118] J.-C. Lei, A. Kutana, B. I. Yakobson, Predicting stable phase monolayer Mo$_2$C (MXene), a superconductor with chemically-tunable critical temperature, J. Mater. Chem. C 5 (2017) 3438–3444.

[119] J.-J. Zhang, S. Dong, Superconductivity of monolayer Mo$_2$C: the key role of functional groups, J. Chem. Phys. 146 (2017) 034705.

[120] Y.-D. Fu, B. Wang, Y. Teng, X.-S. Zhu, X.-X. Feng, M.-F. Yan, P. Korzhavyi, and W. Sun, The role of group III E elements in Nb$_n$AC$_3$ MAX phases (A = Al, Si, Ga, Ge) and the unusual anisotropic behavior of the electronic and optical properties, Phys. Chem. Chem. Phys. 19 (2017) 15471–15483.

[121] C. Ling, L. Shi, Y. Ouyang, J. Wang, Searching for highly active catalysts for hydrogen evolution reaction based on O-terminated MXenes through a simple descriptor, Chem. Mat. 28 (2016) 9026–9032.

[122] G. Gao, A. P. O’Mullane, A. Du, 2D MXenes: A new family of promising catalysts for the hydrogen evolution reaction, ACS Catal. 7 (2016) 494–500.

[123] N. K. Chaudhari, H. Jin, B. Kim, and D. S. Baek, S. H. Joo, K. Heon, M. W. Barsoum, Y. Gogotsi, Interfacial engineering of layered carbides and carbonitrides, Nature commun. 4 (2013) 1716.

[124] J.-C. Lei, A. Kutana, B. I. Yakobson, Predicting stable phase monolayer Mo$_2$C (MXene), a superconductor with chemically-tunable critical temperature, J. Mater. Chem. C 5 (2017) 3438–3444.

[125] J.-J. Zhang, S. Dong, Superconductivity of monolayer Mo$_2$C: the key role of functional groups, J. Chem. Phys. 146 (2017) 034705.

[126] Y.-D. Fu, B. Wang, Y. Teng, X.-S. Zhu, X.-X. Feng, M.-F. Yan, P. Korzhavyi, and W. Sun, The role of group III E elements in Nb$_n$AC$_3$ MAX phases (A = Al, Si, Ga, Ge) and the unusual anisotropic behavior of the electronic and optical properties, Phys. Chem. Chem. Phys. 19 (2017) 15471–15483.

[127] A. VahidMohammadi, A. Hadjikhani, S. Shahbazmohamadi, M. Baidaghi, Two-dimensional vanadium carbide (MXene) as a superconductor with chemically-tunable critical temperature, J. Mater. Mater. Chem. C 5 (2017) 1135–1144.

[128] A. VahidMohammadi, A. Hadjikhani, S. Shahbazmohamadi, M. Baidaghi, Two-dimensional vanadium carbide (MXene) as a superconductor with chemically-tunable critical temperature, J. Mater. Mater. Chem. C 5 (2017) 1135–1144.

[129] Q. Tang, Z. Zhou, P. Shen, Are MXenes promising Anode materials for Li ion batteries? Computational studies on electronic properties and Li storage capability of Ti$_2$C and Ti$_2$C$_2$ (X = F, OH) monolayer, J. Am. Chem. Soc. 135 (2013) 15966–15969.

[130] O. Mashitalir, M. Naguib, V. N. Mochalin, Y. Dall’Agnese, M. Heon, M. W. Barsoum, Y. Gogotsi, Interfacial engineering of layered carbides and carbonitrides, Nature commun. 4 (2013) 1716.

[131] D. Er, J. Li, M. Naguib, Y. Gogotsi, V. B. Shenoy, Ti$_2$C MXene as high capacity electrode material for metal (Li, Na, K, Ca) ion batteries, ACS Appl. Mater. Interfaces 6 (2014) 11173–11179.

[132] Q. Wan, S. Li, J.-B. Liu, First-principle study of Li-ion storage of functionalized Ti$_2$C monolayer with vacancies, ACS Appl. Mater. Interfaces 10 (2018) 6169–6177.

[133] Y. Aierken, C. Sevik, O. Glseren, F.M. Peeters, D. Cakir, MXenes/graphene heterostructure for Li battery applications: a first principles study, J. Mater. Chem. A. 6 (2018) 2337–2345.

[134] X. Liu, X. Shao, F. Li, M. Zhao, Anchoring effects of S-terminated Ti$_2$C MXene for lithium-sulfur batteries: A first-principles study, Appl. Surf. Sci. 455 (2018) 522–526.

[135] D. Rao, L. Zhang, Y. Wang, Z. Meng, X. Qian, J. Liu, X. Shen, G. Qiao, R. Lu, Mechanism of the improved performance of lithium sulfur batteries with MXene-based additives, J. Phys. Chem. C. 121 (2017) 11047.

[136] Y. Xie, Y.Dall’Agnese, M. Naguib, Y. Gogotsi, M. W. Barsoum, H. L. Zhuang, L. Zhuang, P. R. C. Kent, Prediction and characterization of MXene nanosheet anodes for non-Lithium ion batteries, ACS Nano 8 (2014) 9606–9615.

[137] Y.-X. Yu, Prediction of mobility, enhanced storage capacity, and volume change during sodiation on interlayer-expanded functionalized Ti$_2$C$_2$ MXene anode materials for sodium-ion batteries, J. Phys. Chem. C. 120 (2016) 5288–5296.

[138] X. Chen, Z. Kong, N. Li, X. Zhao, C. Sun, Proposing prospects of Ti$_2$CN transition metal carbides (MXenes) as anode in Li-ion battery: a DFT study, Phys. Chem. Chem. Phys. 18 (2016) 32937–32943.

[139] D. Wang, Y. Gao, Y. Liu, D. Jin, Y. Gogotsi, X. Meng, F. Du, G. Chen, Y. Wei, First-principles calculations of Ti$_2$N and Ti$_2$NT$_2$ (T = O, F, OH) monolayers as potential anode materials for Lithium-ion batteries and beyond, J. Phys. Chem. C 121 (2017) 13025–13034.

[140] J. Hu, B. Xu, C. Ouyang, S.A. Yang, Y. Yao, Investigations on V$_2$C and V$_2$C$_2$ (X = F, OH) monolayer as a promising anode material for Li ion batteries from first-principles calculations, J. Phys. Chem. C. 118 (2014) 24274–24281.

[141] L. Bai, H. Yin, X. Zhang, Energy storage performance of V$_2$C$_2$ MXene monolayer as electrode material studied by first-
principles calculations, RSC Adv. 6 (2016) 54999–55006.

[142] D. Sun, Q. Hu, J. Chen, X. Zhang, L. Wang, Q. Wu, A. Zhou, Structural transformation of MXene (V2C, Cr2C and Ta2C) with O groups during lithiation: A first-principles investigation, ACS Appl. Mater. Interfaces 8 (2016) 74.

[143] J. Zhu, A. Chronopou, U. Schwinghamerschlgl, Nb-based MXenes for Li-ion battery applications, Phys. Status Solidi RRL 9 (2015) 726–729.

[144] L. Bai, H. Yin, L. Wu, X. Zhang, First-principle study of the Nb41C2T2 systems as electrode materials for supercapacitors, Comput. Mater. Sci. 143 (2018) 225–231.

[145] F. Li, C. R. Cabrera, J. Wang, Z. Chen, A Cr2CO2 monolayer as a promising cathode for lithium and non-lithium ion batteries: a computational exploration, RSC Adv. 6 (2016) 81591–81596.

[146] X. Zou, G. Li, Q. Wang, D. Tang, B. Wu, X. Wang, Energy storage properties of selectively functionalized Cr-group MXenes, Comput. Mater. Sci. 150 (2018) 236–243.

[147] Q. Sun, Y. Dai, Y. Ma, T. Jing, W. Wei, B. Huang, Ab initio prediction and characterization of MoC monolayers as anodes for lithium-ion and sodium-ion batteries, J. Phys. Chem. Lett. 7 (2016) 937–943.

[148] I. Persson, J. Halim, H. Lind, T. W. Hansen, J. B. Wagner, L.-Å Näslund, V. Darakchieva, J. Palissaitis, J. Rosen, and P. O. Å. Persson, 2D transition metal carbides (MXenes) for carbon capture, Adv. Mater. (2018), 1805472. DOI: 10.1002/adma.201805472.

[149] E. Lee, A. VahidMohammadi, B. C. Prorok, Y. S. Yoon, M. Beidaghi, and D. J. Kim, Room temperature gas sensing of two-dimensional titanium carbide (MXene), ACS Appl. Mater. Interfaces 9 (2017) 37184.

[150] X.-F. Yu, Y.-C. Li, J.-B. Cheng, Z.-B. Liu, Q.-Z. Li, W.-Z. Li, X. Yang, B. Xiao, Monolayer Ti2CO2: A promising candidate for NH3 sensor or capture with high sensitivity and selectivity, ACS Appl. Mater. Interfaces 7 (2015) 13707–13713.

[151] A. Junkaew, R. Arróyave, Enhancement of the selectivity of MXenes (M2C, M = Ti, V, Nb, Mo) via oxygen-functionalization: Promising materials for gas-sensing and separation, Phys. Chem. Chem. Phys. 20 (2018) 6073–6082.

[152] S. Ma, D. Yuan, Z. Jiao, X. Dai, Monolayer Sc2CO2: A promising candidate as a SO2 gas sensor or capture, J. Phys. Chem. C. 121 (2017) 24077–24084.

[153] Q. Hu, D. Sun, Q. Wu, H. Wang, L. Wang, B. Liu, A. Zhou, J. He, MXene: A new family of promising hydrogen storage medium, J. Phys. Chem. A. 117 (2013) 14253–14260.

[154] Q. Hu, H. Wang, Q. Wu, X. Ye, A. Zhou, D. Sun, L. Wang, B. Liu, J. He, Two-dimensional Sc2C: A reversible and high-capacity hydrogen storage material predicted by first-principles calculations, Int. J. Hydrogen Energy 39 (2014) 10606–10612.

[155] A. Yadav, A. Dashora, N. Patel, A. Miotello, M. Press, D.C. Kothari, Study of 2D MXene Cr2C4, ACS Appl. Mater. Interfaces 6 (2014) 88–95.

[156] X. Sang, Y. Xie, M.-W. Lin, M. Alhabeb, K. L. V. Aken, Y. Gogotsi, P. R. C. Kent, K. Xiao, and R. R. Unocic, Atomic defects in monolayer titanium carbide (Ti2C2xTx) MXene, ACS Nano 10 (2016) 9193–9201.

[157] S. Zhao, W. Kang, and J. Xue, MXene nanoribbons, J. Mater. Chem. C 3 (2015) 879.

[158] Q. Xu, L. Ding, Y. Wen, W. Yang, H. Zhou, X. Chen, J. Street, A. Zhou, W.-J. Ong, and N. Li, High photoluminescence quantum yield of 18.7% by using nitrogen-doped Ti3C2 MXene quantum dots, J. Mater. Chem. C 6 (2018) 6360–6369.

[159] A. Kakelkani and S. Isamil-Beigi, Polarization-driven catalysis via ferroelectric oxide surfaces, Phys. Chem. Chem. Phys. 18 (2016) 19676–19695.