Tuning the Basal Plane Functionalization of Two-Dimensional Metal Carbides (MXenes) To Control Hydrogen Evolution Activity

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Supporting Information

ABSTRACT: Hydrogen evolution reaction (HER) via electrocatalysis is one method of enabling sustainable production of molecular hydrogen as a clean and promising energy carrier. Previous theoretical and experimental results have shown that some two-dimensional (2D) transition metal carbides (MXenes) can be effective electrocatalysts for the HER, based on the assumption that they are functionalized entirely with oxygen or hydroxyl groups on the basal plane. However, it is known that MXenes can contain other basal plane functionalities, e.g., fluorine, due to the synthesis process, yet the influence of fluorine termination on their HER activity remains unexplored. In this paper, we investigate the role and effect of basal plane functionalization (Tn) on the HER activity of 5 different MXenes using a combination of experimental and theoretical approaches. We first studied Ti3C2Tn produced by different fluorine-containing etchants and found that those with higher fluorine coverage on the basal plane exhibited lower HER activity. We then controllably prepared Mo2CTn with very low basal plane fluorine coverage, achieving a geometric current density of −10 mA cm−2 at 189 mV overpotential in acid. More importantly, our results indicate that the oxygen groups on the basal planes of Mo2CTn are catalytically active toward the HER, unlike in the case of widely studied 2H-phase transition metal dichalcogenides such as MoS2, in which only the edge sites are active. These results pave the way for the rational design of 2D materials for either the HER, when minimal overpotential is desired, or for energy storage, when maximum voltage window is needed.

KEYWORDS: MXene, electrocatalysis, 2D material, hydrogen evolution, basal plane activation

INTRODUCTION

The realization of a sustainable energy economy calls for environmentally friendly and economical methods to generate fuels, preferably utilizing sunlight as the most abundant energy source on Earth. Molecular hydrogen (H2) is an ideal target product as it can be used directly as fuel,3 or stored and distributed in industrial scale.7 Additionally, H2 is also a key raw material in the chemical industry including its use in ammonium fertilizer synthesis crucial for worldwide food production. Broadly, there are two ways to obtain H2 sustainably: via a direct photovoltaic electrolysis approach,3−5 Critical to both approaches is the development of efficient, robust, and cost-effective HER electrocatalysts. Two-dimensional (2D) transition metal dichalcogenides (TMDs) like MoS2 have been widely studied as non-precious-metal catalysts for the HER.5−9 Unfortunately, with the exception of a less stable 1T-phase,10−12 it has been shown that only the edge sites of the thermodynamically stable 2H-phase of TMDs are active for HER catalysis.13 To maximize the density of edge sites in TMDs, intricate materials preparation, complex architecture design, and/or hybridization with other materials are often required, limiting their widespread use in large scale catalytic H2 production.14−17

A large family of 2D layered materials called MXenes with the general formula Mnx+1Xn−1Tn (n = 1−3, M = early transition metal, e.g., Mo and/or Ti, X = C and/or N) has emerged and showed promise in many applications.18,19 MXenes are usually synthesized by selectively etching away the “A-element” atoms of ternary or quaternary layered metal carbides/nitrides, such as MAX phases (Mnx+1AXn), resulting in functional groups T (e.g., O, OH, F) present on the basal planes of MXenes.18,20

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Due to their high surface area, high electronic conductivity, hydrophilic nature, and ease of production, MXenes are finding their way into a myriad of applications including energy storage, lithium/multivalent-ion batteries, pseudocapacitors, electromagnetic interference shielding, etc. When it comes to electrocatalysis, previous theoretical and experimental studies have shown that some members of the MXene family are promising catalysts for the HER. However, these studies were conducted with the assumption that the basal plane functional groups T are composed exclusively of O or OH groups. As MXenes are usually obtained by selective etching of MAX phases using F-containing etchants such as HF and LiF−HCl, the introduction of F terminations on the basal plane is inevitable and other terminations, such as Cl, may be present. In some cases like Ti3C2Tx, a significant basal plane F functionalization (in excess of 20 at %) has been shown to alter its electronic properties. Therefore, to develop truly active and robust MXene HER catalysts with precise control over their overpotential and stability, it is crucial to understand the influence of basal plane functionalization.

In this work, we investigate the role and effect of F termination on the HER activity of 5 distinct MXenes with different Ti to Mo stoichiometries, using a combination of experimental and theoretical approaches. First, by studying Ti3C2Tx synthesized using different F-containing etchants, we found that those with a higher F coverage on the basal plane exhibited lower HER activity. This is consistent with theoretical calculations which show that substitution of F in place of O terminations on the basal plane results in increased HER overpotential compared to the fully O-functionalized case. Our computational investigation predicts a lowering in the HER performance upon O to F functionalization not only for Ti-based MXenes such as Ti3C2Tx and Ti2CTx, but also for Mo-based ones such as Mo2CTx, Mo2TiC2Tx, and Mo2Ti2C3Tx. In the latter two MXenes, Mo is occupying the outer atomic layers, controlling their electrochemical behavior. With this important insight, we synthesized Mo2CTx MXene with very low F basal plane coverage, which was found to be an active and stable HER catalyst in acid (189 mV overpotential to reach a geometric current density of −10 mA cm−2). More importantly, both theoretical and experimental results show that the basal planes of Mo2CTx are catalytically active toward the HER.

### RESULTS AND DISCUSSION

First, Ti3C2Tx MXene was selected to illustrate the effects of F functionalization on the HER activity, as this particular Ti-based MXene can be synthesized using etchants with varying concentration of F, namely, 50 and 10 wt % HF, and LiF−HCl mixture (more details can be found in Supporting Information Section 1). We observed the characteristic lamellar structure for the Ti3C2Tx samples synthesized with HF etchant solution (Figure 1a, Figure S1a) while a more compact structure was obtained with LiF−HCl etchant (Figure S1c). Consistent with previous observations, we observed a slight shift of the (0002) X-ray diffraction (XRD) reflection to a lower angle for the LiF−HCl etched Ti3C2Tx samples as compared to the HF etched ones (Figure 1b, Figure S1b,d). This corresponds to a c-lattice parameter of 32.8 Å for the LiF−HCl etched Ti3C2Tx, compared to the HF etched ones (Figure 1b, Figure S1b,d). The expansion of the c-lattice parameter was previously attributed to a difference in surface functionalization or stacking, or different numbers of intercalated layers of water.

We characterized the electrochemical HER performance of Ti3C2Tx by using linear sweep voltammetry (LSV) at a scan...
Figure 2. Comparison between theory and experiment for Ti3C2Tx with different functional groups on the basal plane: (a) DFT calculated HER overpotential as a function of F coverage on the basal plane (F:Ti ratio) for Ti3C2T, with experimental HER overpotentials at $-10 \text{ mA cm}^{-2}$ in 0.5 M H2SO4 electrolyte overlaid. Dashed line is a linear fit to the experimental data set. The basal plane is fully covered with F when F:Ti is 0.67. (b) LSVs of Ti3C2T, 50% HF performed in 0.5 M H2SO4 and 0.1 M KOH electrolytes, and treated with 0.01 M KOH (prior to LSV scans in 0.5 M H2SO4 electrolyte).

Figure 3. Characterization of Ti- and Mo-based MXenes: (a) DFT calculated HER overpotential as a function of F coverage on the basal plane (F:Mo or F:Ti ratio). There are no data points for Mo2TiC2T and Mo2Ti2C3T at 100% F coverage, and no data points for Mo2CT, at 50%, 75%, and 100% F coverage due to desorption as described in the text. (b) SEM micrograph and (c) XRD pattern of Mo2CT. (d) LSVs and (e) Tafel plot of MXenes in 0.5 M H2SO4 electrolyte. (f) Comparison between theoretical and experimental overpotential (at $-10 \text{ mA cm}^{-2}$) after taking into account the F coverage on the basal plane. Dashed line is a representation of an ideal condition where experimental overpotential coincides with theoretical values.
rate of 10 mV s^{-1}. The catalysts were examined in a three-electrode electrochemical cell using a rotating disk electrode at 1600 rpm in 0.5 M H2SO4 (mass loading: 1 mg cm^{-2} geo unless otherwise stated). The measurements show that the MXenes exhibit the following order with respect to the HER activity: LiF → HCl > 10% HF > 50% HF (Figure 1c). Their experimental overpotentials at a geometric current density of −10 mA cm^{-2} geo were measured to be 538, 767, and 891 mV, respectively. The large Tafel slopes displayed by the Ti3C2T_x samples (128–190 mV dec^{-1}, Figure 1d) indicate that the adsorption of H (Volmer step) could be rate limiting.39 Estimates based on electrochemical capacitance measurements (Figure S2, Table S1) suggest that the Ti3C2T_x samples obtained using different etchants possess similar electrochemical surface areas (ECSA, within a factor of 2.6), which could not account for the large differences in the HER overpotential. In fact, when the current densities are normalized to ECSA, the same HER activity trend holds: LiF > HCl > 10% HF > 50% HF (Figure S2c). Therefore, an estimate of F functional groups on the basal plane was made by measuring the elemental F to Ti ratio between the F 1s and the Ti 2p that belongs to the MXene (Figure S3, Table S2), as determined using X-ray photoelectron spectroscopy (XPS). Consistent with previous reports, the F:Ti ratio of the Ti3C2T_x materials follows the order LiF > HCl < 10% HF < 50% HF.2,32,33 Note that this trend shows the opposite order to the HER activity of the MXenes (Figure 1c), suggesting that the HER activity of Ti3C2T_x can be greatly attenuated by the presence of F.

To further investigate the undesirable effect of F functionalization of the basal plane on the HER activity, we performed density functional theory (DFT) calculations to determine the change in free energy for H adsorption (ΔG_H) in the absence and presence of different quantities of F functional groups on the basal plane (DFT calculation details in Supporting Information, Section 7). It is well-established that calculated ΔG_H values can be used to estimate the HER activity of a catalyst, with one criterion for an ideal HER catalyst being a ΔG_H value that is close to zero.40–43 First, by considering the adsorption of O and OH at each adsorption site [bridge, atop, face centered cubic (fcc) hollow, and hexagonal closed packed (hcp) hollow], we determined the most favorable basal plane coverage of Ti3C2T_x to be fully O-terminated (i.e., Ti3C2O2x) at zero applied potential. Next, by studying the adsorption of H, we calculated the ΔG_H value of Ti3C2O2 at 0.038 eV, which is achieved when H is adsorbed on the O atoms located on the fcc hollow sites (Figure S4, Table S3). When F functional groups were gradually introduced to substitute the O terminations [corresponding to F basal plane coverages of 0%, 25%, 50% and 75% (i.e., Ti3C2F0.5O1.5 → Ti3C2FxO1.5 → Ti3C2F2xO0.5, with F:Ti ratios of 0, 0.17, 0.33, and 0.50 per unit cell respectively], the ΔG_H was found to increase monotonically with the F surface coverage (Figure 2a). We find that the preferred H adsorption site is atop the O termination independent of the O:F ratio as long as there is O present on the basal planes. For the cases when H is adsorbed on top of the O functional group, the influence of other nearby F terminations on the H adsorption is weak. When all O species on the basal plane are fully replaced with F functional groups (i.e., Ti3C2F2 with F:Ti ratio of 0.67), the most favorable H adsorption site cannot be O anymore, and it inevitably becomes atop F. The significant jump in the ΔG_H value to >1.48 eV at 100% F coverage (Figure 2a) is therefore attributed to the change in the active site from atop O to atop F. The experimental HER overpotentials at −10 mA cm^{-2} geo for Ti3C2T_x with different F:Ti ratios generally match the trend obtained from the DFT calculations (Figure 2a). A similar trend was found for another Ti-based MXene, Ti3C2T_x, in which the ΔG_H increases monotonically from 0% to 75% F surface coverage, and then rises rapidly at 100% F coverage (Figure 3a).

We further conducted experiments to alter the F surface functionalization of all three Ti3C2T_x samples postsynthesis and measured their HER performance. This is achieved by treating the samples in 0.01 M KOH for 30 min prior to LSV scans (Supporting Information, Section 1.3), which is expected to reduce the basal plane coverage of F,44 but does not alter the MXene morphology or structure significantly (Figure S1e,f). XPS measurements indicate that the F:Ti ratio for Ti3C2T_x 50% HF sample decreased significantly from 0.46 to 0.28 after the KOH treatment. Strikingly, the HER overpotential at −10 mA cm^{-2} geo decreased by 274 mV after the KOH treatment (Figure 2b), indicating that the presence of F terminations on the basal plane is indeed deleterious for the HER. Similar HER improvement was also achieved by conducting the HER LSV in 0.1 M KOH electrolyte, with 251 mV lower HER overpotential at −10 mA cm^{-2} geo compared to the measurement in 0.5 M H2SO4 (Figure 2b, see also Supporting Information, Section 8, for additional discussion). Comparable results were also obtained for the Ti3C2T_x 10% HF sample, where a KOH treatment and KOH electrolyte improved the HER overpotential by 90 and 155 mV, respectively (Figure S5a). However, no improvement in HER activity was observed for the Ti3C2T_x LiF > HCl sample after KOH treatment (Figure S5b), possibly because the untreated LiF > HCl etched sample already had low amounts of F termination to begin with (Table S2).

On the basis of the key finding that the HER activity is highly dependent on the type and coverage of surface functional groups for Ti-based Ti3C2T_x MXene with different terminations, we extend the investigation to Mo-based MXenes, including Mo2CT_x, Mo2TiC2T_x and Mo2Ti2CT_x. Prior studies have shown that mixed Mo–Ti MXenes (Mo2TiC2T_x and Mo2Ti2CT_x) are more energetically favorable when the outer metal layers consist of Mo and the inner layers consist of Ti.5,24 Using the same DFT calculation approach as outlined above for the Ti-based MXenes, we here utilized a (2 × 2) O-functionalized Mo-MXene supercell, and systematically replaced one side of the MXene basal plane O terminations with F. We find that while the Ti-based MXenes (with Ti on the basal plane, Ti3C2T_x and Ti2CT_x) have both O and F preferring to be on the fcc hollow site (calculated on a (1 × 1) surface), MXenes with Mo on the basal plane (Mo2CT_x, Mo2TiC2T_x, and Mo2Ti2CT_x) show slightly more complicated behavior: the F initially prefers to be in the hcp hollow sites when O is present, but then switch to the fcc hollow site at one full monolayer F coverage.

As in the case of Ti3C2T_x and Ti2CT_x, we found that partial substitution of O with F increased the ΔG_H of the Mo-based MXenes with respect to the fully O-functionalized basal plane (Figure 3a). For Mo2TiC2T_x and Mo2Ti2CT_x, increasing the F surface coverage from 0% to 25% (F:Mo ratio of 0 to 0.25) results in a notable increase in ΔG_H. Intriguingly, there are no ΔG_H data points for Mo2Ti2CT_x and Mo2TiC2T_x at 100% F coverage (F:Mo ratio of 1). This is because, at these F coverages, there is no stable H adsorbed on the surface. We
found that initiating H adsorption on the F terminations results in the formation of highly unstable HF species which desorb from the surface, instead of evolving H2. It is noteworthy that Mo2CT with 0% F surface coverage exhibits a ΔG_H value of 0.048 eV (Figure 3a), lower than that calculated for 2H-phase MoS2 (0.08 eV).40 Thus, in theory, Mo2CT should be an excellent HER catalyst. However, increasing the F surface coverage of Mo2CT from 0% to 25% increases the ΔG_H drastically from 0.048 to 0.714 eV (there are no ΔG_H data points at 50%, 75%, and 100% F coverage for the reasons described above). Thus, controlling the F basal plane functionalization of the Mo2CT at the synthesis stage is extremely important for its use as an efficient HER catalyst.

With this insight, we controllably synthesized Mo2CT, Mo2TiC2Tx and Mo2Ti2CTx with low F coverages on the basal plane through careful etching of their parent MAX phases: Mo2Ga2C, Mo2TiAlC2, and Mo2Ti2AlC3, respectively (Figure S6). Mo-based MXenes show more compact layers compared to Ti-based ones (Figure 3b, Figure S7), with a c-lattice parameter of around 19.9 Å, as inferred from the diffraction data (Figure 3c). Because of the weaker Mo−F bond strength compared to Ti−F,45,46 these Mo-based MXenes were found to have very low F basal plane coverages, with F:Mo ratios ranging from 0.02 to 0.05 as estimated using XPS. When evaluated for their HER activity, the Mo2CTx, Mo2TiC2T_x, and Mo2Ti2C3T_x MXenes were found to be active HER catalysts in 0.5 M H2SO4. Their HER activity follows the order Mo2CTx > Mo2TiC2T_x > Mo2Ti2C3T_x, regardless of whether the current densities are normalized by geometric area or by ECSA (Figure 3d, Figure S2d). It is noteworthy that Mo2CTx is an active HER catalyst in acid, requiring 189 mV overpotential to reach −10 mA cm−2geo (Figure 3d, see also Figure S8 for average turnover frequency values). This HER figure of merit is comparable to other nanosheet catalysts reported previously (Table S4). The Tafel slope of Mo2CTx (75 mV dec−1, Figure 3e) was also much lower than that of the
Ti3C2 MXenes (128–190 mV dec−1). A comparison plot was then constructed to relate the theoretical overpotentials (determined from calculated ΔG(H) values) with the experimental overpotentials (measured at −10 mA cm−2) as shown in Figure 3f. In general, we find good agreement between the theoretical and experimental HER overpotentials when F coverage on the basal plane is taken into consideration.

Finally, we turn our attention to Mo2CT x, which shows the lowest HER overpotential among the 5 MXenes investigated. First, we assessed its long-term stability using accelerated cyclic voltammetry (CV) and galvanostatic polarization.37 Comparison of Mo2CT x before and after 1000 CV cycles at HER relevant potentials (between 0.2 to −0.25 V vs RHE) shows almost overlapping curves and negligible change in overpotential (Figure 4a). Furthermore, XPS analysis shows practically unchanged intensity of Mo 3d peaks associated with Mo−C before and after HER, which is consistent with its stable HER performance (Figure S9a). On the other hand, the peaks associated with Mo-oxydized species (Mo5+/6+) decreased in intensity, which could result from reduction under cathodic HER potentials or dissolution in acid. Galvanostatic polarization measurements also indicate that the overpotential to produce H2 at −10 mA cm−2 as on Mo2CT x is very stable for at least 2 h, a common practice for benchmarking in the HER field (Figure S9b).37

Notably, our DFT calculations show that, for all the MXenes investigated in this work, the HER active sites are the O surface functional groups on the basal planes. This is unlike in the case of widely studied 2H-phase TMDs such as MoS2, in which only the edge sites are active.13 Commercial 2H-phase MoS2 with similar morphology and geometric mass loading was found to exhibit much poorer HER activity per geometric area compared to Mo2CT x (Figure 4a, Figure S10). To confirm our theoretical prediction of basal plane activity in MXenes, we first compared the HER activity of Mo2CT x with its parent MAX phase Mo2Ga2C, which contains intercalated Ga atoms between the Mo2C layers instead of O functional groups on the Mo2C layers. Mo2CT x was found to exhibit much higher HER activity compared to that of Mo2Ga2C, with 134 mV lower overpotential to reach −10 mA cm−2 (geo) (Figure 4b), suggesting that the O terminations in the basal plane of Mo2CT x are the active sites, in line with our theoretical predictions.

To test the hypothesis further, comparison with delaminated Mo2CT x was also performed. The HER performance of the MXenes is expected to improve when more layers are delaminated from each other, exposing significantly more basal plane area per gram of catalyst and hence more active sites. After delamination, Mo2CT x showed very thin layers with a smooth surface that is translucent to electron microscopy (Figure 4c), with a 3-fold increase in ECSA as estimated using capacitance measurements (Table S1). Compared to pristine Mo2CT x, the delaminated Mo2CT x showed higher HER activity with a 27 mV smaller overpotential at −10 mA cm−2 (geo) (Figure 4d), as well as an increase in average turnover frequency (Figure S8).

Finally, to demonstrate that the basal planes are indeed catalytically active, we also exposed Mo2CT x to prolonged ultrasonication. Ultrasonication is one of the most commonly used methods to induce damage to the basal planes and maximize the number of edge sites of TMDs using a high powered burst from the liquid–vapor interface.38 After 1 h of ultrasonication under controlled temperature (4−5 °C) and protective atmosphere (N2), we observed that the Mo2CT x particles broke into much smaller pieces, with a significant fraction of damaged basal planes (dotted lines and circles, Figure 4e). The selected area electron diffraction (SAED) inset shows that the expected pattern of Mo2CT x with in-plane a-lattice parameter of 2.509 Å, is retained after ultrasonication. The HER overpotential of ultrasonicated Mo2CT x with damaged basal planes degraded to 482 mV at −10 mA cm−2 (geo) (Figure 4f), which is 293 mV larger than that of pristine Mo2CT x. Taken together, our findings demonstrate that the basal planes of Mo2CT x are the active sites for the HER. Moreover, this work also explains why Ti3C2T x, MXene50 has a much wider voltage window compared to a Mo2CT x supercapacitor in acidic electrolyte.50 MXenes that are not promising for HER applications may be the best ones for use in aqueous supercapacitors,50 when the largest possible overpotential is required.

CONCLUSION

We have shown, through a combination of DFT calculations, electrochemical analysis, and an array of characterization methods, that the presence of F terminations on the basal planes of Ti-based MXenes is detrimental to their HER performance. A clear relationship was established, linking the degree of F termination and departure from the ideal HER overpotential where the surface is fully O-terminated. We have shown that the adverse effect of F surface functionalization is not exclusive to Ti-based MXenes, but can be used to explain the HER activity of Mo-based ones as well. Further detailed investigations of the Mo2CT x MXene revealed that the origin of its excellent HER activity is not related to the parent phase Mo2Ga2C, nor the edge sites like most other 2D TMDs studied for the HER. Rather, the basal planes of the Mo2CT x were found to be active for the HER. Our findings highlight that MXenes, with properly functionalized HER active basal planes, are promising electrocatalysts as they contain no precious metals, are easy to synthesize, and do not require additional laborious materials preparation, such as hybridization with other materials and/or complex architecture design, which is typically required for other 2D materials like 2H-phase MoS2 to bring out optimal HER activity. Moreover, this work provides guidance for the rational selection of promising materials for other electrochemical applications, such as supercapacitors used in aqueous electrolytes.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsaem.7b00054.

Materials synthesis, materials characterization, electrochemical measurements, estimation of electrochemical surface area, X-ray photoelectron spectroscopy data, density functional theory calculations, estimation of average turnover frequency, performance comparison, and stability assessment (PDF)

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