Two-Dimensional Molybdenum Carbide (MXene) as an Efficient Electrocatalyst for Hydrogen Evolution

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Supporting Information

ABSTRACT: The hydrogen evolution reaction (HER) is an important energy conversion process that underpins many clean energy technologies including water splitting. Herein, we report for the first time the application of two-dimensional (2D) layered transition metal carbides, MXenes, as electrocatalysts for the HER. Our computational screening study of 2D layered M2XnTn+1 (M = metal; X = (C, N); and Tn = surface functional groups) predicts Mo2CTx to be an active catalyst candidate for the HER. We synthesized both Mo2CTx and Ti2CTx MXenes, and in agreement with our theoretical predictions, Mo2CTx was found to exhibit far higher HER activity than Ti2CTx. Theory suggests that the basal planes of Mo2CTx are catalytically active toward the HER, unlike in the case of widely studied MoS2, in which only the edge sites of the 2H phase are active. This work paves the way for the development of novel 2D layered materials that can be applied in a multitude of other clean energy reactions for a sustainable energy future.
supercapacitors,\textsuperscript{30,31} Li and multivalent ion batteries,\textsuperscript{32,33} and as electrocatalysts for the oxygen evolution reaction.\textsuperscript{34} A most recent theoretical study suggested the potential of V\textsubscript{2}C MXene as an effective HER catalyst due to doping;\textsuperscript{35} however, there have been no experimental studies to date that explore the application of MXenes as electrocatalysts for the HER.

Herein, we report for the first time a combined theoretical and experimental study of MXenes as electrocatalysts for the HER. We computationally screened a set of M\textsubscript{2}X\textsubscript{T\textsubscript{x}} materials (M = Sc, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, and W; X = C and N; and T\textsubscript{x} = H, O, OH, and H\textsubscript{2}O) to determine their hydrogen adsorption free energy (\(\Delta G_{\text{H}}\)) and expected overpotential for HER catalysis, thereby identifying several promising HER catalyst candidates. We experimentally synthesized and measured the electrochemical HER activity of two of the MXene materials investigated computationally, Mo\textsubscript{2}CT\textsubscript{x} and Ti\textsubscript{2}CT\textsubscript{x}. In agreement with our theoretical predictions, Mo\textsubscript{2}CT\textsubscript{x} was found to exhibit far higher HER activity than Ti\textsubscript{2}CT\textsubscript{x}. We further found Mo\textsubscript{2}CT\textsubscript{x} to exhibit stability in acid during galvanostatic HER measurements, indicating a promising catalyst system.

To understand trends in HER activity among MXenes, we performed a computational screening study by means of density functional theory (DFT) calculations to determine \(\Delta G_{\text{H}}\), which has been shown to be a descriptor of HER activity to a first approximation.\textsuperscript{6,17,36-39} We first established the most probable functional groups (T\textsubscript{x}) present on each MXene sheet at zero applied potential. We investigated the adsorption of 1 ML of H, O, OH, and H\textsubscript{2}O at each adsorption site and on each side of the (1 × 1) MXene sheet; the adsorption sites include bridge, ontop, fcc, and hcp (Figure 1a), for a total of 16 distinct adlayers per MXene (four types of sites with four possible adsorbates). The functional group atoms and the MXene lattice were allowed to relax (see the Supporting Information for details). Next, we performed a Pourbaix diagram analysis by comparing the lowest free energy of each coverage to determine the full ML coverage. We found that a full ML of O as the functional group is the lowest free energy for all of the studied MXenes except for Sc\textsubscript{2}C and Sc\textsubscript{2}N\textsubscript{2}, for which a full ML of OH corresponds to the lowest free energy (Table S1).

Once the most probable surfaces, that is, the most favorable functional groups, were identified under relevant HER conditions, we utilized the relaxed structures, doubled the x and y directions to make a (2 × 2) supercell, and studied the adsorption of H on the new lattice. It is well-known that a necessary (but insufficient) condition for an active HER catalyst is one with a \(\Delta G_{\text{H}}\) that is closest to thermoneutral.\textsuperscript{6,17,36-39} We adapted the following procedure to determine the HER overpotential: If the \(\Delta G_{\text{H}}\) was positive, we found the optimum coverage at zero potential. If not, we continued adding H to the system until \(\Delta G_{\text{H}}\) became positive. For Sc\textsubscript{2}C and Sc\textsubscript{2}N\textsubscript{2}, we also tried to remove the H from OH\textsubscript{*} to make an adsorbed O\textsuperscript{*}. The smallest \(\Delta G_{\text{H}}\) at the optimum coverage is given in Table S1. For Sc\textsubscript{2}C and Sc\textsubscript{2}N\textsubscript{2}, the lowest \(\Delta G_{\text{H}}\) is a result of removing H from the surface, to turn an OH\textsubscript{*} to an O\textsuperscript{*}; for Hf\textsubscript{2}N\textsubscript{2}, V\textsubscript{2}N\textsubscript{2}, and W\textsubscript{2}N\textsubscript{2}, the lowest \(\Delta G_{\text{H}}\) originates from adsorbing H to a metal ontop site; for all other MXenes, the lowest \(\Delta G_{\text{H}}\) comes from adding H to turn an O\textsuperscript{*} to an OH\textsuperscript{*} (where * indicates an adsorbed species).

A purely DFT-calculated HER volcano plot is presented in Figure 1b, showing the wide range of HER activity expected for carbide- and nitride-based MXenes. Although \(\Delta G_{\text{H}}\) varies largely from −1.5 to 1.5 eV, most of the MXenes fall on the weak-binding side of the volcano (the right leg), indicating generally weak interactions with H among the MXenes. On the basis of their adsorption properties, we find that the MXenes can be viewed in three distinct categories: (1) the lowest free energy adsorption site for O is the fcc site for both the carbide and nitride (M = Sc, Ti, Zr, Hf, and V), (2) the lowest free energy adsorption site for O is the hcp site for both the carbide and nitride (M = Cr, Mo, and W), and (3) the lowest free energy adsorption site for O is the fcc site for the carbide but hcp for the nitride (M = Nb and Ta). For cases in which the fcc site is the most favorable O binding site for the carbide (categories 1 and 3), the nitride binds the H more strongly than the carbide (i.e., the nitride is farther to the left on the volcano). However, for cases in which the most favorable O adsorption site of the carbide is the hcp site (category 2), the opposite trend is observed, that is, the nitride binds the H more weakly (i.e., the nitride is farther to the right on the volcano). A
previous study showed the optimal \( \Delta G_{\text{H}} \) on \( \text{V}_2\text{C} \) to be \(-0.37\) eV at 25% H coverage. In our calculation, we see that the smallest \( \Delta G_{\text{H}} \) was found to be 0.201 eV at 37.5% coverage; this coverage was not considered by the previous study.

Figure 1c shows a zoom-in of the top of the volcano, revealing several promising HER catalyst candidates’ theoretical overpotentials of <0.2 V, including the functionalized carbides \( \text{Sc}_2\text{C} \) and \( \text{Mo}_2\text{C} \) and nitrides \( \text{V}_2\text{N} \), \( \text{Hf}_2\text{N} \), and \( \text{Nb}_2\text{N} \). For comparison, the theoretical HER overpotential of the edge of \( \text{MoS}_2 \) was calculated to be \(<0.1\) V.\(^5\) For all of the MXenes, the O* on the basal plane is the active site, with the exceptions of \( \text{Hf}_2\text{N}, \text{V}_2\text{N}, \text{and W}_2\text{N} \), in which the catalytically active site is the ontop metal site. Among the \( \text{M}_2\text{X} \) materials predicted to be catalytically active for the HER based on the computational analysis, in some cases such as \( \text{Sc}_2\text{C} \) and \( \text{Hf}_2\text{N} \), their synthesis
has not yet been reported, whereas for others such as the Mo$_2$C MXene, the successful synthesis has recently been realized.

Experimentally, we synthesized and assessed the HER activity of Mo$_2$CT$_x$ and Ti$_2$CT$_x$. Briefly, Mo$_2$CT$_x$ and Ti$_2$CT$_x$ MXenes were synthesized by HF etching of their parent ternary carbides, Mo$_2$GaC and Ti$_2$AlC, by removing the Ga and Al atoms, respectively (Figure 2a; see the Supporting Information for details).

The synthesis procedure results in surface functional groups $T_x$ on the basal planes of the MXenes. The X-ray diffraction (XRD) patterns of Mo$_2$CT$_x$ and Ti$_2$CT$_x$ show relatively broadened and downshifted (0002) peaks compared to their precursors, indicating an increase in their $c$-lattice parameters ($c$-LPs) and smaller domain sizes in the [0001] direction (Figures 2d and S1c). Comparing the (0002) peak positions reveals that both materials have similar $c$-LP at 20.1 Å, suggesting that, although the starting precursors have different $c$-LPs, the resulting MXenes have similar interlayer spacing (Figures 2e and S1c).

To evaluate electrocatalytic activities for the HER, we first drop-cast Mo$_2$CT$_x$ and Ti$_2$CT$_x$ onto glassy carbon electrodes (mass loading: 0.1 mg cm$^{-2}$) using Nafton as a binder. These materials were then examined in a three-electrode electrochemical cell using a rotating disk electrode apparatus at 1600 rpm in 0.5 M H$_2$SO$_4$(aq) (see the Supporting Information for details). Figure 3a shows the anodic-going iR-corrected linear sweep voltammograms (LSVs) for bare glassy carbon, Ti$_2$CT$_x$, and Mo$_2$CT$_x$. The bare glassy carbon shows no measurable activity within the potential window of interest. Ti$_2$CT$_x$ exhibit a small $iR$ in 0.5 M H$_2$SO$_4$(aq) (see the Supporting Information for details).

The TOF$_{avg}$ of Mo$_2$CT$_x$ was estimated using four peaks, two of which are doublets corresponding to Mo$^{5+}$/6+, respectively, arising from surface oxidation of the catalyst. After HER testing of Mo$_2$CT$_x$, we see that the two doublets corresponding to Mo$^{5+}$/6+ remained relatively unchanged, which is consistent with the stable activity of the catalysts (Figure 3c). On the other hand, there was a noticeable decrease in intensity of the doublets corresponding to oxidized Mo species (Mo$^{5+}$/6+), which could result either from reduction of the oxidized species under cathodic HER potentials or from dissolution of those species in acid. We also show that functionalized Mo$_2$C and Ti$_2$C are more stable than either of their constituent elements or bulk carbides, showing that the functionalized MXenes are stable and will not decompose to their constituent elements or combine to form their bulk carbides (see the Supporting Information for details).

To evaluate the stability of Mo$_2$CT$_x$ and Ti$_2$CT$_x$, we performed a galvanostatic hold at 10 mA cm$^{-2}$ and measured the temporal evolution of the potential over 2 h, a common practice for catalyst benchmarking in the HER field. As shown in Figure 3b, no significant change in overpotential was observed for either Mo$_2$CT$_x$ or Ti$_2$CT$_x$. Figure S2c shows anodic-going iR-corrected LSVs for both Mo$_2$CT$_x$ and Ti$_2$CT$_x$ before and after the galvanostatic stability measurement. Interestingly, while Ti$_2$CT$_x$ showed no significant change in overpotential during the galvanostatic hold, the HER activity as measured by cyclic voltammetry decreased further (Figure S2c). For Mo$_2$CT$_x$, the anodic-going iR-corrected LSV after the galvanostatic hold overlaps the stable LSV from before the galvanostatic hold (Figure S2c), further highlighting the stability of Mo$_2$CT$_x$ in an acidic environment. X-ray photoelectron spectroscopy (XPS) was also carried out to investigate the changes in chemical state of Mo$_2$CT$_x$ before and after HER testing (Figure 3c). The Mo 3d spectrum of the as-synthesized Mo$_2$CT$_x$ can be fitted using four peaks, two of which are doublets corresponding to Mo$^{4+}$/5+, respectively, arising from surface oxidation of the catalyst. After HER testing of Mo$_2$CT$_x$, we see that the two doublets corresponding to Mo$^{4+}$/5+ remained relatively unchanged, which is consistent with the stable activity of the catalysts (Figure 3c). On the other hand, there was a noticeable decrease in intensity of the doublets corresponding to oxidized Mo species (Mo$^{5+}$/6+), which could result either from reduction of the oxidized species under cathodic HER potentials or from dissolution of those species in acid. We also show that functionalized Mo$_2$C and Ti$_2$C are more stable than either of their constituent elements or bulk carbides, showing that the functionalized MXenes are stable and will not decompose to their constituent elements or combine to form their bulk carbides (see the Supporting Information for details).

To shed some light on the intrinsic per-site activity of Mo$_2$CT$_x$ and Ti$_2$CT$_x$, we calculated average turnover frequencies (TOF$_{avg}$s) based on the theoretical surface coverages of both materials, taking all of the O atoms as the active sites, irrespective of their accessibility; this led to a conservative estimate of the TOF$_{avg}$ (see the Supporting Information for details). The TOF$_{avg}$ of Mo$_2$CT$_x$ was estimated to be $\sim$0.01 Hz s$^{-1}$ at a 200 mV overpotential, much higher than that of Ti$_2$CT$_x$, which requires a $\sim$500 mV overpotential to reach a similar TOF$_{avg}$ (Figure S4). In an effort to improve electrode activity, we also prepared Mo$_2$CT$_x$ in its delaminated form ($d$-Mo$_2$CT$_x$), which has a larger proportion of basal planes exposed (Figure 4a). The increase in the exposed basal plane surface area of $d$-Mo$_2$CT$_x$ was supported by cyclic voltammetry measurements, which indicated higher specific capacitance and hence larger electrochemically active surface area (Figure S5).

As expected, the $d$-Mo$_2$CT$_x$ electrode showed improved HER activity compared to that of Mo$_2$CT$_x$, in terms of both electrode geometric activity (Figure 4b) and TOF$_{avg}$ found to increase to 0.02 Hz s$^{-1}$ at a 200 mV overpotential (Figure S4). This suggests that the basal planes of $d$-Mo$_2$CT$_x$ are indeed catalytically active. Although this TOF$_{avg}$ value is lower than that reported for transition metal sulfi des/phosphides, we note that this is a conservative estimate based on mass loading. Further work is ongoing to determine a more accurate TOF$_{avg}$ value based on more controlled electrodes. We envision that...
the activity of d-Mo2CT\textsubscript{x} can be enhanced through further optimization of the catalyst material, for example, by designing 3D architectures, supporting it on high surface area carbon, or tuning the surface functional groups appropriately.\textsuperscript{15}

In conclusion, we report that MXene materials can be active and stable catalysts for the HER in acid, examined by both electrochemical measurements, turnover frequency, electrochemically active surface area, Table S1, and Figures S1–S5 (PDF).

**Author Contributions**

Y.Z.W.S. and K.D.F. contributed equally to this work.

**Notes**

The authors declare no competing financial interest.

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