Predicting the Electrochemical Synthesis of 2D Materials from First Principles

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ABSTRACT: We show that Pourbaix diagrams generated by combining first principles and tabulated experimental data can determine the electrochemical conditions needed to synthesize metastable phases in solution. As an example, we investigate the synthesis of two-dimensional transition-metal carbides and nitrides (M2Xenes) from their M2AX phase precursors and observe good agreement between the predicted synthesis conditions and those used for existing M2Xenes. In addition, we prescribe synthesis conditions to increase the yields of certain M2Xenes and possibly even enable the synthesis of new M2Xenes. Our results show that the general stability of nitride M2Xenes is not dramatically different from their carbide counterparts, but that most of their experimentally available precursors are more difficult to etch initially because of their more inert A elements.

INTRODUCTION

Acid etching is one of several techniques available for creating two-dimensional (2D) materials.1−4 This process is typically performed by immersing a layered bulk precursor in an acid chosen to selectively remove layers of sacrificial atomic species from among other layers. The newly exposed surfaces of the remaining 2D layers might be passivated by species in solution,5 and often bind to one another through weak dispersion forces.6

Theory and modeling have become indispensable tools for predicting the stability of new 2D materials7−11 and their synthesis through methods like mechanical exfoliation12,13 or chemical vapor deposition.14,15 For synthesis via acid etching, the aqueous environment presents additional challenges for accurate modeling by first-principles approaches.16,17

Here, we present a first-principles framework to characterize the acid etching process of bulk precursor compounds and predict the synthesis conditions for the formation of 2D materials. Our consideration includes applied electric potentials, which are often ignored as a degree of freedom during experimental synthesis. This allows us to investigate the effects of the chosen acid and its concentration, the potential in solution, and the choice of the bulk precursor compound from first-principles calculations. As a benchmark and example of the framework’s usage, we investigate the synthesis of several MXenes, a well-studied class of 2D materials that has been synthesized by acid etching.4,6,8,18−25

MXENES

MXenes are 2D transition-metal carbides and nitrides that can be etched from layered ceramics known as MAX phases.26−30 These ceramics derive their name from their chemical formula M+n+1AXn, where M is an early transition metal, A a group 12−16 element, X carbon or nitrogen, and n generally ranges from 1 to 3. The specific cases discussed in this work are all for n = 1, and we will use the term M2Xenes for this subclass. Figure 1a shows an example crystal structure for the V2AlC MAX phase. Due to their compositional flexibility, the list of experimentally available MAX phases is quite large and growing.31

When certain MAX compounds are immersed in an aqueous HF solution or in other solvents with active F− ions,22,23 the acid selectively attacks the M−A bonds, often forming AF3 compounds, which diffuse out from among M+n+1Xn layers. These M+n+1Xn layers are immediately passivated by species coming from the solution, especially oxygen,5 to form a final stoichiometry close to M+n+1XnO2. At this point during the
investigate the aqueous stability of several nonsolid solution referred to as M₂Xenes and M₂AX phases, respectively. On the formation energies obtained from the NIST NBS tables in position products in solution. We utilize the experimental ionic pH phase, diagrams, which illustrate which species are This formalism enables the construction of Pourbaix, or pE/ microscopes for investigations of aqueous etching processes. We use the experimental data and density-functional theory (DFT), which provides a new theoretical solution by combining experimental data and density-functional theory (DFT), which provides a new theoretical framework for calculating formation energies of ions and molecules in standard DFT. For dissolved species for which the NBS tables do not contain data, we use values from Pourbaix’s 1966 Atlas. We extract formation energies from these references for all molecules containing E=O, E=H, and E=O−H, where E is repeated for each of the M, A, and X elements. We also add molecules with compositions containing fluorine, since it is also present in the experimental etching solutions.

We employ the formation energies for standard conditions, G₀, to calculate the Gibbs free energy, Gᵣ, of each species, i, in solution

\[ Gᵣ (i, pH, φ) = G₀ⁱ + 0.0591 \log cᵢ - nₒμ \mu H₂O \]

\[ + pH (n_H - 2n₀) + φ (−n_H + 2nᵢ + qᵢ) \]

where \( cᵢ \) is the concentration of species \( i \), \( n₀ \) and \( n_H \) are the respective numbers of oxygen and hydrogen atoms in the species, \( pH H₂O \) is set to the formation energy of water at \( −2.46 \) eV, \( φ \) is the electric potential, and \( qᵢ \) is the species’ charge. We select a moderate concentration of \( 10^{-3} \) M for all ionic species and solid phases, \( i \), and their dependence on pH and potential, \( φ \), we construct the Pourbaix diagram as the convex hull connecting the formation energies of all compounds and species, just like any other phase diagram.

**DFT Calculations.** The energies of all solid compounds are calculated using DFT with the Vienna ab initio simulation package (VASP). To obtain an accuracy of about 1 meV/atom, we use a plane-wave basis with a cutoff energy of 500 eV and sample the reciprocal spaces with a Monkhorst–Pack mesh with a density of 1000 k-points per atom.

While in solution, M₂Xenes exist as dispersion-bound multilayer structures and not free-standing nanosheets. Their accordion-like morphologies typically contain dozens of individual layers. Therefore, the energies of the M₂Xenes are calculated using fully periodic structures to account for the binding interaction among neighboring layers. Dispersion-corrected optB88 functionals are used to accurately capture the interlayer interactions in these structures.

**Correction to Experimental Formation Energies.** To bridge the compatibility gap between experimental formation energies and DFT-calculated formation energies, we employ the linear correction scheme of Persson et al. In this formalism, experimental formation energies of ions are shifted by the difference between the DFT and experimental formation energies of a reference compound (preferably a simple binary oxide) containing the same element as the ion. For example, the correction factor applied to the formation energies of all ions containing Nb is calculated as

\[ \Delta \mu_{Nb}^{corr} = \frac{1}{2} [E_DFT (Nb₂O₅) − E_exp (Nb₂O₅)] \]

where Nb₂O₅ is the reference compound and the factor 1/2 normalizes the correction per Nb atom. The experimental formation energies, \( E^{exp} \), are taken for all binary oxides from ref [3181] DOI: 10.1021/acs.jpcc.8b10802 J. Phys. Chem. C 2019, 123, 3180–3187
We apply this correction additively for each atom in a molecule or molecular ion.

**Potentials of Zero Charge.** The intrinsic electric potential at a neutral metallic surface in solution, or the potential of zero charge (PZC), is often nonzero. This is an important effect to consider in etching processes because it can create local potentials at the precursor surface where the etching reactions occur, even when no external potential has been applied. Therefore, the PZC can be used to determine the relevant region of the Pourbaix diagram for an experimental etching reaction carried out without any external field.

To obtain PZC values for M2AX surfaces, we calculate the Fermi level of M-terminated M2AX slabs in an implicitly modeled solvent. The PZC is equal to the difference between the Fermi level of the slab and the potential in the bulk of the solvent with respect to the standard hydrogen electrode (SHE).

We use the implicit solvation model VASPsol55,56 with an aqueous electrolyte of permittivity εr = 78.4 and a Debye length of 2 Å, and a slab thickness of 11 atomic layers, separated by 30 Å of the solvent. The SHE potential calculated using VASPsol is 4.6 V. With these settings, we obtain the PZC values that are shown as horizontal dashed lines in the Pourbaix diagrams below.

**Stability Criteria.** The successful synthesis of a M2Xene by electrochemical etching of a M2AX phase requires two conditions to be fulfilled. First, the solution must be able to etch the A element from the M2AX phase. This can be observed by the instability of the M2AX phase in the Pourbaix diagram and the formation of A–F ions. These ions typically precipitate as AF salts during experimental synthesis, as illustrated in Figure 1. The second condition is that the remaining M2XO2 layers must not dissolve in the solution. In other words, the overall reaction should proceed as

\[
M_{2}AX + 2H_{2}O + nHF 
\rightarrow M_{2}XO_{2}(MXene) + nF_{2} + \frac{4 + n}{2}H_{2}
\]  

These two criteria can be investigated simultaneously by creating a Pourbaix diagram with the M2AX phase and the M2Xene as its only two solid phases. Any regions in this diagram where the M2AX phase is unstable against dissolution and where the M2Xene is stable against dissolution indicate conditions under which the synthesis reaction should proceed.

We refer to these partial Pourbaix diagrams that contain only the two solid phases of interest as "etching" diagrams to distinguish between them and complete Pourbaix diagrams that contain all thermodynamically stable solid phases. Diags of this nature can be generated to illustrate any electrochemical etching process for which the expected initial and final stable or metastable compounds are known.

## RESULTS AND DISCUSSION

**Benchmarking the Stability of Existing M2Xenes.** Figure 2 illustrates the application of this approach to the synthesis of the Ti2CO2 M2Xene by electrochemical etching of the Ti2AlC M2AX precursor. Ti2CO2 has been experimentally synthesized by etching Ti2AlC in aqueous HF solutions of 0.5 M concentration, which have a pH of about 1.5.18 There is a large region of stability for Ti2CO2 in the diagram, indicating the wide range of conditions under which this 2D material is stable. Additionally, there are no solution conditions where the Ti2AlC precursor will not be etched.

The experimental conditions (pH = 1.5 and 0 V applied potential) are very near to the left edge of the predicted Ti2CO2 stability region, but with the PZC value for this system around −0.6 V, we expect that Ti2CO2 may not immediately be stable in the experimental solution near the Ti2AlC surface. This could explain why synthesis attempts have achieved only 60% Ti2CO2 yield. If we assume that the other 40% of the possible yield dissolves into solution, the ionic concentration and pH values in solution will increase as the etching progresses.

Figure 3 shows how the stability region for Ti2CO2 grows in size as the ionic concentration is increased from 10−3 to 10−1 M, following Le Châtelier’s principle and eq 1. We therefore anticipate that Ti2CO2 becomes increasingly stable as the etching reaction progresses and that etching solutions preconditioned with high ion concentrations may increase Ti2CO2 yield.

In addition to Ti2CO2, two other carbide M2Xenes (not including solid solutions) have been synthesized from M2AX phases to date: Nb2CO2 and V2CO2.21 Both of these were etched from A = Al M2AX phases.

The etching diagram for Nb2CO2 is illustrated in Figure 4. Figure 4 shows a wide range of stability at negative potentials. At low pH, the potential where Nb2CO2 becomes stable (−0.6 V) is quite

![Diagram of the etching process](image-url)

**Figure 2.** Etching diagram for Ti2AlC, showing a region of stability for Ti2CO2. For clarity, only Ti- and C-containing ions are labeled in the diagrams. The composition including other ions (e.g., Al- and F-based ions) changes for every facet in the diagram (regions enclosed by the solid white lines). The dashed black line indicates the PZC, and the dashed gray lines indicate the stability range for water.

**Figure 3.** Regions of stability for Ti2CO2 at three different ion concentrations of 10−3, 10−2, and 10−1 M.

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close to its calculated PZC of \(-0.4\) V, meaning that even without the application of an external potential, the reaction is expected to take place in 0.5 M HF solutions. This agrees well with the observed experimental yields of close to 100% for this M\textsubscript{2}Xene.\textsuperscript{21}

Figure 5a shows that V\textsubscript{2}CO\textsubscript{2} is only stable at higher pH when using an ion concentration of \(10^{-3}\) M. Similar to the case of Ti\textsubscript{2}CO\textsubscript{2}, this could explain why V\textsubscript{2}CO\textsubscript{2} yields were only around 60% in the initial report of its synthesis.\textsuperscript{21} Figure 5b shows the etching diagram for V\textsubscript{2}AlC using projected experimental conditions after considerable dissolution; at an ion concentration of 0.1 M, the stability region for V\textsubscript{2}CO\textsubscript{2} indeed spreads into acidic pH values between 3 and 4, reaffirming the reduced yield and delayed onset of successful etching for this material.

A small amount of the Mo\textsubscript{2}CO\textsubscript{2} M\textsubscript{2}Xene was synthesized\textsuperscript{38} by etching a Mo\textsubscript{2}Ga\textsubscript{2}C nanolaminate\textsuperscript{57} similar to the Mo\textsubscript{2}GaC M\textsubscript{2}AX phase. Mo\textsubscript{2}GaC has not been successfully etched, so the exfoliation of Mo\textsubscript{2}Ga\textsubscript{2}C to form a M\textsubscript{2}Xene nanosheet is a promising result, which broadens the possibilities of M\textsubscript{2}Xene synthesis from off-stoichiometry M\textsubscript{n+1}AX phases.

The etching diagrams for Mo\textsubscript{2}GaC and Mo\textsubscript{2}Ga\textsubscript{2}C in Figure 6 show that these precursors behave quite similarly and are more difficult to etch than the A = Al precursors shown so far. The main difference between these two is that there is a region in Figure 6b where Mo\textsubscript{2}Ga\textsubscript{2}C and Mo\textsubscript{2}CO\textsubscript{2} are expected to coexist, but no such region exists for Mo\textsubscript{2}GaC under the same conditions.

The actual Mo\textsubscript{2}CO\textsubscript{2} yields were not provided in the report of its synthesis, but significant amounts of an unetched precursor were observed in the final solution along with Mo\textsubscript{2}CO\textsubscript{2}\textsuperscript{38} in good qualitative agreement with the coexistence region in Figure 6b. We also highlight that the PZC is slightly lower for Mo\textsubscript{2}Ga\textsubscript{2}C than for Mo\textsubscript{2}GaC, which may also help to stabilize Mo\textsubscript{2}CO\textsubscript{2} as it forms. Our results confirm that Mo\textsubscript{2}Ga\textsubscript{2}C is a better precursor than Mo\textsubscript{2}GaC, but that 100% yields for either precursor may be difficult to achieve.

Our predictions for these systems indicate that these diagrams can capture successful experimental etching conditions with an estimated accuracy around pH \(\pm 1\) and \(\pm 0.5\) V.
The etching diagrams for (a) Ti$_2$AlN and (b) V$_2$GaN and their respective M$_2$Xenes. The PZC values are shown by the dashed black lines.

**Nitride M$_2$Xenes.** The etching diagrams of nitride, or X = N, M$_2$Xenes are of particular interest because these materials are more difficult to synthesize. Nitride M$_2$Xenes also have electronic and mechanical properties considerably different from their carbide counterparts, meaning that their synthesis opens up a new range of accessible properties in the M$_2$Xene family. So far only two nitride MXenes, Ti$_2$NO$_2$ and Ti$_2$N$_2$O$_2$, have been synthesized directly in solution, both from their A = Al MAX phases. The list of experimentally known nitride M$_2$AX phases includes Ti$_2$AlN, Ti$_2$GaN, Ti$_2$InN, V$_2$GaN, Cr$_2$GaN, Zr$_2$InN, Zr$_2$TlN, and Hf$_2$SnN. We calculate and show etching diagrams for Ti$_2$AlN and V$_2$GaN in Figure 7.

The etching diagram for Ti$_2$AlN in Figure 7a displays a large stability region for Ti$_2$NO$_2$. This does not immediately explain why Ti$_2$NO$_2$ could not originally be synthesized using 5, 10, or 20% HF solutions, but it does indicate that this M$_2$Xene can exist as a metastable phase in acidic solutions. This is in agreement with later successful attempts at synthesis using hydrochloric acid and potassium fluoride. The formation of anatase TiO$_2$ was observed in the unsuccessful synthesis attempts using HF etchants, meaning that nitride M$_2$Xenes must be carefully protected from excessive oxidation during synthesis. We have intentionally excluded TiO$_2$, which is known to be the ground state for titanium in water under most conditions, from our diagrams to show the possibility of metastable phases forming. If it is included, it replaces Ti$_2$NO$_2$ everywhere it appears in the diagram.

Similar to Mo$_2$GaC, V$_2$GaN in Figure 7b still displays a large region of stability for the M$_2$AX phase at low potentials close to its calculated PZC where no etching is expected to occur. The appearance of this large M$_2$AX phase stability region for A ≠ Al is observed for other systems as well, confirming that A = Al M$_2$AX phases are generally the best precursors for etching. Unfortunately, Ti$_2$AIN is the only such X = N M$_2$AX phase currently in existence. We expect that the lack of A = Al precursors is at least partly responsible for the rarity of nitride M$_2$Xenes. We also note that V$_2$NO$_2$ and Mo$_2$NO$_2$ were very recently synthesized by ammoniation of their carbide M$_2$Xene counterparts, a synthesis route that circumvents the need for an A = Al, X = N precursor and may prove to be successful for a number of other nitride M$_2$Xenes.

**Aqueous Stability of New M$_2$Xenes.** Cr- and Ta-Based M$_2$Xenes. Cr$_2$AlC exists as a precursor from which a new Cr$_2$CO$_2$ M$_2$Xene could potentially be synthesized. The etching diagram generated for this system in Figure 8a shows only a small window of stability for Cr$_2$CO$_2$ at pH > 9. Similar to those of Ti$_2$CO$_2$ and V$_2$CO$_2$, this region grows with increasing ion concentration, but not as dramatically. Still, it is possible that some yield of Cr$_2$CO$_2$ could be achieved by carefully etching Cr$_2$AlC at moderate pH and high ion concentrations.

Ta$_2$AlC, in Figure 8b, displays a flat stability region for Ta$_2$CO$_2$ at potentials below −1.25 V and dissolves to form TaO$_2$ everywhere else in the diagram. The PZC for Ta$_2$AlC is actually slightly positive (0.08 V), so it is likely that an external potential would need to be applied to the solution to successfully etch Ta$_2$AlC into Ta$_2$CO$_2$. Such a strong potential is well outside the range of water’s stability, however, and may therefore lead to other more complex dissociation processes.

Sc-, Zr-, and Hf-Based M$_2$Xenes. We find that no M$_2$Xenes based on Sc, Zr, and Hf have any stability against dissolution in their precursor etching diagrams, even at high ionic concentrations. For Sc-based M$_2$Xenes, the Sc atoms dissolve into solution to form Sc$_3^{3+}$ ions at pH < 4 and ScOH$_2^{+}$ ions at pH > 4. Zr atoms from Zr-based M$_2$Xenes are predicted to primarily form HZrO$_2^{3+}$ ions in solutions with negative potentials. Similarly, Hf atoms will readily form HO$_2^{5+}$ in solution. All of these dissolution reactions show in the diagrams even at ion concentrations up to 1 M. Therefore, none of these M$_2$Xenes are predicted to be viable using aqueous etching, regardless of the acid or the precursor used. This also means that these M$_2$Xenes, even if synthesized by alternative means, are unsuitable for aqueous applications, including photocatalysis. Thicker and more stable n = 2 Hf$_2$C$_2$O$_7$ and Zr$_2$C$_2$O$_7$ MXenes, however, were recently synthesized by etching layered compounds similar to MAX phases.
CONCLUSIONS

We have developed a method by which the electrochemical synthesis of MXenes can be predicted using partial Pourbaix diagrams. This method can be generalized to apply to any class of materials under investigation as precursors for etching 2D materials or other metastable phases.

Specifically, the etching diagrams offer solution conditions that may enhance the yields of etching reactions of existing Ti$_2$CO$_2$ and V$_2$CO$_2$ M$_2$Xenes and may enable the synthesis of new M$_2$Xenes compounds, including Cr$_2$CO$_2$ and Ta$_2$CO$_2$. In general, we recommend preconditioning etching solutions with high concentrations of metallic ions to inhibit the dissolution of metallic M$_2$Xene surfaces and thereby increase the final M$_2$Xene yield.

Importantly, the diagrams generated for nitride M$_2$Xenes show that some are metastable in acidic solutions, but the A elements, e.g., Ga, in many of their experimentally available precursors are more difficult to etch than Al. This offers an explanation why nearly all MXenes have been electrochemically synthesized from A = Al precursors to date.

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