Supplementary Information

Intercalation and Delamination of Layered Carbides and Carbonitrides

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Supplementary Fig. S1. X-ray diffraction analysis of intercalated f-Ti$_3$C$_2$ MXene. X-ray diffraction (XRD) patterns of f-Ti$_3$C$_2$ MXene: i) before treatment, ii) after hydrazine monohydrate (HM) treatment in dimethylformamide (DMF) at 80 °C, iii) after HM treatment at 80 °C; (iv) after HM treatment in DMF at 80 °C; and at room temperature (v). Patterns i-iii: initial MXene was dried at 100 °C for 22 h before intercalation. Patterns iv-v: as-received wet MXene was used as an initial material. The resulting powders were washed with DMF after intercalation.
Supplementary Figure S2. X-ray photoelectron spectroscopy analysis of intercalated f-Ti$_3$C$_2$. (a,b) X-ray photoelectron spectroscopy spectra of f-Ti$_3$C$_2$ intercalated with hydrazine monohydrate (HM) at 80 °C for 24 h (a) and with HM and dimethylformamide at 80 °C for 24 h (b). Both insets show N1s peaks for corresponding samples. (c) Ti 2p from f-Ti$_3$C$_2$ with HM (same as in (a)), (d) O 1s from f-Ti$_3$C$_2$ with HM and DMF (same as in (b)).
Supplementary Figure S3. Intercalation of f-MXenes using hydrazine monohydrate. X-ray diffraction patterns of (i) f-Ti$_3$CN MXene before (black) and after (red) HM treatment and (ii) f-TiNbC MXene before (blue) and after (green) HM treatment. For all samples, initial MXene was dried in a desiccator under vacuum (< 10 Torr).
Supplementary Figure S4. Molecular dynamics simulations. (a) Representative molecular dynamics (MD) snapshots of 4x2x1 f-Ti$_3$C$_2$ MXene supercells with 8 and 12 molecules of N$_2$H$_4$. Carbon is shown in dark grey, titanium in light grey, oxygen in red, nitrogen in blue, hydrogen in white. When the number of intercalated N$_2$H$_4$ molecules increases from 0 to 14, the density (Supplementary Fig. S4b) and the $c$-lattice parameter of the supercell change in a non-linear, stepwise fashion (Fig. 3a). Analysis of MD trajectories reveals that the steps are due to the onset, formation, and completion of N$_2$H$_4$ monolayers. The transition from monolayer to bilayer of intercalate is observed in the structure with 8 N$_2$H$_4$ molecules while the supercell with 12 N$_2$H$_4$ in the interlayer space of MXene shows distinct bilayers of the intercalate molecules. (b) Density evolution of 4x2x1 MXene supercell intercalated with different numbers of N$_2$H$_4$ molecules. (c) Energy evolution of 4x2x1 MXene supercell with 6 molecules of N$_2$H$_4$ showing that the energy is conserved during the MD run.
Supplementary Figure S5. Intercalation of f-Ti$_3$C$_2$ with dimethyl sulfoxide and urea. X-ray diffraction patterns of f-Ti$_3$C$_2$: i) before any treatment, ii) after DMSO treatment taken 30 min (blue) and 3 weeks (red) after storing in a desiccator at room temperature, iii) after urea treatment. Both initial and intercalated f-MXenes were dried in a desiccator under vacuum (< 10 Torr).
Supplementary Figure S6. Schematic of delamination of MXene flakes.
Supplementary Figure S7. The galvanostatic charge/discharge curves at a 1C rate. The “y” value shown on top x-axis was calculated assuming a MXene chemistry of Ti$_3$C$_2$(OH)$_2$. 
Supplementary Figure S8. Bottom part of the Universal Force Field optimized structure of α-Ti₃AlC₂ unit cell. The interatomic distances shown and lattice parameters of the optimized structure are compared to the literature data in Supplementary Table S2. In this figure carbon is shown in dark grey, titanium in light grey, aluminum in pink.
Supplementary Tables

Supplementary Table S1. Sheet resistivity, resistivity and density of cold-pressed discs for different non-intercalated MXenes and MXenes treated with hydrazine monohydrate (HM).

<table>
<thead>
<tr>
<th>MXene</th>
<th>Sheet Resistivity, Ω/□</th>
<th>Resistivity, Ω m</th>
<th>Density, g/cm³</th>
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<tbody>
<tr>
<td></td>
<td>Non-intercalated</td>
<td>HM treated</td>
<td>Non-intercalated</td>
</tr>
<tr>
<td>Ti₃C₂</td>
<td>61</td>
<td>243</td>
<td>0.016</td>
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<tr>
<td>Ti₃CN</td>
<td>43</td>
<td>711</td>
<td>0.011</td>
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<tr>
<td>Nb₂C</td>
<td>321</td>
<td>12806</td>
<td>0.139</td>
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<tr>
<td>TiNbC</td>
<td>230</td>
<td>44661</td>
<td>0.092</td>
</tr>
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Supplementary Table S2. Structural parameters of $\alpha$-Ti$_3$AlC$_2$

<table>
<thead>
<tr>
<th>Parameter</th>
<th>This work (UFF)</th>
<th>Literature $^{40}$</th>
<th>Difference, % $^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice parameters $a$ and $b$ (Å)</td>
<td>3.250</td>
<td>3.023-3.087</td>
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<tr>
<td>Lattice parameter $c$ (Å)</td>
<td>19.607</td>
<td>18.287-18.652</td>
<td>+6.2</td>
</tr>
<tr>
<td>$d_{Ti-C}$ (Å)</td>
<td>2.177</td>
<td>2.082</td>
<td>+4.6</td>
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<tr>
<td>$d_{Ti-Ti}$ (Å)</td>
<td>2.974</td>
<td>2.966</td>
<td>+0.3</td>
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<tr>
<td>$d_{C-C}$ (Å)</td>
<td>3.250</td>
<td>3.082</td>
<td>+5.5</td>
</tr>
</tbody>
</table>

$^a$ The difference is calculated as

\[
\frac{(Value_{\text{This work}} - Average \ value_{\text{Literature}})}{Average \ value_{\text{Literature}}} \cdot 100
\]
**Supplementary Discussion**

**XPS analysis.** The high resolution XPS spectrum of Ti 2p for HM-treated f-Ti$_3$C$_2$ is shown in Supplementary Figure S2c. The Ti(0), Ti(II), and Ti(IV) peaks indicate the presence of titanium oxides (II, IV) and titanium carbide. Also in Supplementary Figure S2d, high resolution XPS spectrum of O 1s show the presence of hydroxyl groups as well as Ti-O in the HM/DFM-treated f-Ti$_3$C$_2$.

It is worth mentioning that the XPS data we reported previously in Ref. 17 contain inaccurately labeled peaks and numbers; the peak of Ti(0) 2p3/2 corresponding to Ti-C is at 454.5 eV, while Ti(IV) 2p1/2 peak corresponding to Ti-O is at 464.6 eV. Also the OH peak was observed at 531.7 eV in the O 1s, while the Ti-O was observed at 530.3 eV.

**Supplementary Methods**

**Materials.** The following chemicals were used: titanium aluminum carbide, 211, (Ti$_2$AlC, > 92 wt.% purity, 3-ONE-2, Voorhees, USA), titanium carbide (TiC, 99 wt.% purity, Johnson Matthey Electronic, New York, USA), hydrofluoric acid (HF, 48-51 wt.%, Acros Organics, Morris Plains, USA), hydrazine monohydrate, HM (N$_2$H$_4$·H$_2$O, > 98.0 wt.% purity, TCI America, Portland, USA), N,N-dimethylformamide, DMF, (≥ 99 wt.%, Acros Organics, Morris Plains, USA), dimethylsulfoxide, DMSO, (≥ 99.7 wt.%, Fisher Scientific, Fair Lawn, USA), urea (> 99 wt.%, Fisher Scientific, Fair Lawn, USA), acetone (≥ 99 wt.%, Acros Organics, Morris Plains, USA), ethyl alcohol (95 wt.%, Decon Laboratories, Inc., King of Prussia, USA) tetrahydrofuran, THF, (≥ 99 wt.%, Acros Organics, Morris Plains, USA), chloroform (99.8 wt.%, stabilized in 0.5-1 % ethanol, Sigma Aldrich, St. Louis, USA), toluene (99.9 wt.%, Fisher Chemical, Fair Lawn, USA), hexane (≥ 99 wt.% Reagent Plus, Sigma Aldrich, St. Louis, USA),
thiophene (≥ 99 wt.%, Sigma Aldrich, St. Louis, USA), formaldehyde (37 % w/w, stabilized with 10 to 15 wt.% methanol, Fisher Chemical, Fair Lawn, USA), poly(1,1-difluoroethylene) (Alfa Aesar, Ward Hill, USA), 1-methyl-2-pyrrolidinone (99.95 wt.%, Alfa Aesar, Ward Hill, USA), lithium hexafluorophosphate (LiPF₆), ethylene carbonate and diethyl carbonate (99.8 wt.%, 99.95 wt.% and 99.98 wt.%, respectively, Novolyte Technologies, Independence, USA). All chemicals were used as received without further purification.

**Synthesis of MXene.** f-MXenes were synthesized by liquid exfoliation of the corresponding MAX phases described previously.¹⁷,¹⁸ Non-sieved Ti₃AlC₂ powder was treated with 50% aqueous HF solution at room temperature (RT), for 22 h. The resulting suspensions were washed five times using deionized water and centrifuged to separate the powder until the pH of the liquid reached ~ 4. A small part of the still wet material was used immediately for intercalation. The rest was dried in a desiccator under vacuum, created by a water jet pump (the pressure in the desiccator was < 10 Torr) at RT for 24 h or in the vacuum oven (~10⁻² Torr) at 100 °C for 22 h, placed into capped glass vials and stored at ambient conditions for further experiments.

**Material preparation.** To intercalate f-Ti₃C₂ with HM, two types of powders were used: i) as-received, washed, wet f-Ti₃C₂ and, ii) the powder prepared as in (i) and additionally dried in a desiccator under vacuum, created by a water jet pump (the pressure in the desiccator was < 10 Torr) at RT for 24 h or in the vacuum oven (~10⁻² Torr) at 100 °C for 22 h. To intercalate f-Ti₃CN and f-TiNbC with HM, both f-MXene powders were previously dried in a desiccator under vacuum (< 10 Torr) at RT for 24 h. To intercalate f-Ti₃C₂ with all other organic compounds (see Methods section), f-Ti₃C₂ powder was dried in a desiccator under vacuum (< 10 Torr) at RT for 24 h.
**Dynamic Light Scattering (DLS) measurements** were performed according the following procedure: A ~1.5 mL of f-MXene, dispersed in water, was transferred in a clear disposable particle size measurement cell (DTS0012, Malvern Instruments, Ltd. Malvern, Worcestershire, UK), equilibrated at 25 °C for 60 s, and then measured with a particle size analyzer (Zetasizer Nano ZS, Malvern Instruments, Ltd.) equipped with 50 mW, 633 nm laser with scattered light been detected at 173° to the direction of the incident light (173° Backscatter NIBS default), which is an optimal geometry for detecting small particles. Each sample was measured three times.

In its original form, used here, DLS approximates particles of any shape by equivalent spheres, therefore it is most suited for particles of nearly spherical shape. For 2D f-MXene flakes the approximation by spheres is quite strained and the “diameter” deduced from these measurements is some average of their lateral dimensions and thickness.

**Gas sorption analysis** was carried out using a Quantachrome Autosorb-1 with nitrogen (N₂), carbon dioxide (CO₂), and Ar adsorbates. Prior to the analysis, the samples were outgassed under vacuum at 200 °C for 48 h. The specific surface area (SSA) was calculated from the volume absorbed at 77 K using the Brunauer-Emmet-Teller (BET) equation. The gas sorption measurements for the d-MXene were carried out on the MXene “paper” that was synthesized by filtering the delaminated MXene suspension as described above. The SSA of the MXene “paper” measured using N₂ was 98 m².g⁻¹, which is significantly higher than SSA before delamination (23 m²·g⁻¹). It is worth noting that the SSA of the “paper” was higher when CO₂ and Ar (128 and 167 m²·g⁻¹ respectively) were used than when N₂ was used which can be explained by the presence of small pores.
**Molecular dynamics (MD) simulations.** The Universal Force Field (UFF) parameters are estimated from simple relations that depend only on the element, its hybridization, and connectivity and are not parameterized by any experimental data. While UFF precision could be inferior to more specialized force fields, we had to trade the accuracy for generality, which is required for the systems considered here. In future, for more precise computational studies, a force field parameterized by experimental data and including the combination of elements and bonds specific for intercalated MXenes should be developed, similar to those developed for clays (e.g., CLAYFF\(^{41}\)).

To validate the force field and the methodology used for computations, we performed geometry optimization of Ti\(_3\)AlC\(_2\) (MAX phase) and compared the optimized structure to the available data. A P\(_{6}\)/mmc space group Ti\(_3\)AlC\(_2\) unit cell was constructed using structural parameters from Ref. \(^{42}\) and then relaxed using UFF, while subjected to an isostatic external pressure of 0.1 MPa (1 atm) and allowing for cell optimization with the following symmetry constrains: \(a=b; \alpha=\beta=90^{\circ}; \gamma=120^{\circ}\). Geometry optimization convergence tolerance parameters (Energy = 0.02 cal/mol, Force = 1 cal/mol/Å, Stress = 1 MPa, Displacement = 0.00001Å) were same as those used for MD simulations (see Methods in the main text). The optimized Ti\(_3\)AlC\(_2\) structure is shown in Supplementary Figure S8. The parameters of this structure are compared to the available literature data in Supplementary Table S2.

From Supplementary Table S2 the differences in structural parameters from the available literature data are in the range 0.3-6.4 %, with all distances and cell parameters computed in this work being slightly larger as compared to the literature data.

We, therefore, used UFF to model hydrazine intercalated MXene.
Supplementary References

40. Shein, I.R. & Ivanovskii, A.L. Graphene-like titanium carbides and nitrides Ti\textsubscript{n+1}C\textsubscript{n}, Ti\textsubscript{n+1}N\textsubscript{n} (n=1, 2, and 3) from de-intercalated MAX phases: First-principles probing of their structural, electronic properties and relative stability. *Comp. Mater. Sci.* **65**, 104-114 (2012).
