

# Supporting Information

## Mechanistic Insight into the Chemical Exfoliation and Functionalization of $\text{Ti}_3\text{C}_2$ MXene

Pooja Srivastava<sup>†,¶</sup>, Avanish Mishra<sup>†,¶</sup>, Hiroshi Mizuseki<sup>‡</sup>, Kwang-Ryeol Lee<sup>‡</sup>, and Abhishek K. Singh<sup>\*†</sup>

<sup>†</sup>Materials Research Centre, Indian Institute of Science, Bangalore-560012

<sup>‡</sup>Center for Computational Science, Korea Institute of Science and Technology (KIST), Seoul, 136-791, Republic of Korea

<sup>¶</sup>These authors contributed equally to this work

---

\*abhishek@mrc.iisc.ernet.in

## Model Structure

In MAX, two MXene layers of  $\text{Ti}_3\text{C}_2$  are interleaved with Al atom. Figure S1 show the model structure for MAX phase considered here for the study of the exfoliation of MXene. Here, the optimized distance between two layers of MXene and the length of Al–Ti bonds are found to be 4.54 Å and 2.86 Å, respectively.

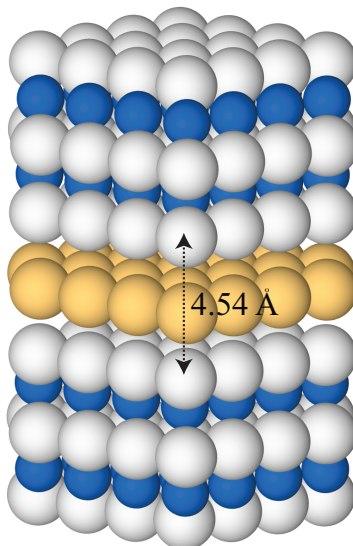


Figure S1: Model MAX Structure of  $\text{Ti}_3\text{AlC}_2$ . Silver, blue, and orange balls represent Ti, C, and Al atoms, respectively.

## Effect of $\text{H}_2\text{O}$

Intercalation of  $\text{H}_2\text{O}$  was considered in  $6 \times 1 \times 1$  MAX structure.  $\text{H}_2\text{O}$  molecule spontaneously dissociates into H and OH and terminates the Ti atoms, also shown in Figure S2.

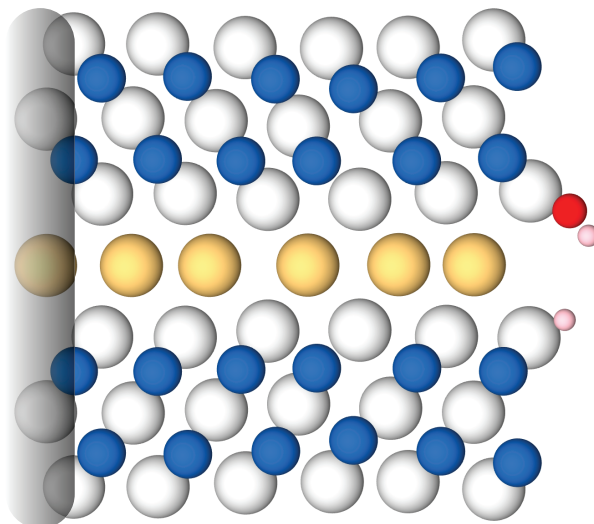


Figure S2:  $\text{H}_2\text{O}$  dissociation at the edge of MAX, and subsequent termination of edge Ti atoms by H/OH. Silver, blue, orange, cyan, red, and pink balls represent Ti, C, Al, F, O, and H atoms, respectively.

## Ab-initio Molecular Dynamics

At 18% HF concentration, the effects of temperature has been considered at two different temperature 300 and 500 K and the dynamics is observed upto 10ps.

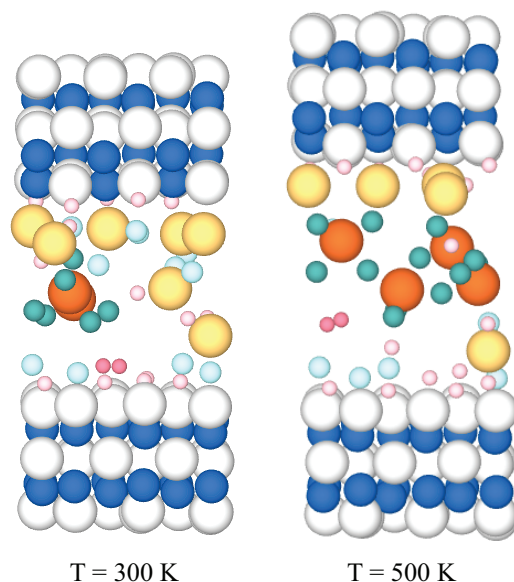


Figure S3: AIMD snapshots at 10ps for two different temperatures 300 and 500 K. Silver, blue, orange, cyan, red, and pink balls represent Ti, C, Al, F, O, and H atoms, respectively. To highlight the Al, F and H atoms forming the  $\text{AlF}_3$  and  $\text{H}_2$  darker shades of respective colours are used.

## Formation Energy

Formation energy of the HF/ $\text{H}_2\text{O}$  intercalated MAX were calculated by using the following equation:

$$E^f = E_{\text{I-Ti}_3\text{AlC}_2} - E_{\text{Ti}_3\text{AlC}_2} - \mu_{\text{I}} \quad (\text{S1})$$

where  $E_{\text{I-Ti}_3\text{AlC}_2}$  and  $E_{\text{Ti}_3\text{AlC}_2}$  are the energies of the MAX phase in the presence and absence of guest species, respectively.  $\mu_{\text{I}}$  is the chemical potential of the functional group terminating the edge Ti atom. Here,  $\mu_{\text{F}}$  and  $\mu_{(\text{OH})}$  are referenced to the total energy of HF and  $\text{H}_2\text{O}$  molecules, respectively.

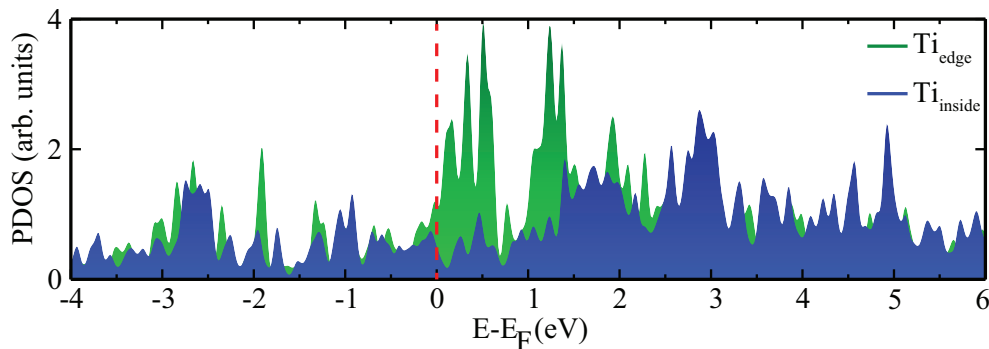


Figure S4: PDOS for Ti-atoms at edge and inside the bulk region of MAX.

## PDOS for edge and bulk Ti atoms

Atom projected density of state (PDOS) analysis (Figure S4) clearly show that, at Fermi level the DOS of Ti edge atom is large relative to that of Ti inside the bulk MAX. It indicates that edge Ti atoms would be more reactive compared to the one which are close to bulk-type region (Figure S4). This can also be observed in Figure 1b, due to increased DOS the F and H binds very strongly with edge Ti atom.

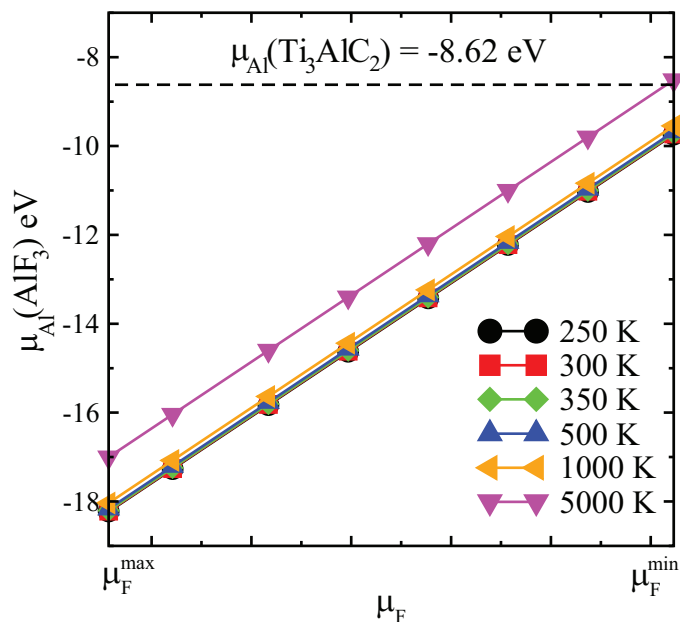


Figure S5: Variation of chemical potential of Al ( $\mu_{\text{Al}}$ ) in  $\text{AlF}_3$  with chemical potential of F ( $\mu_{\text{F}}$ ).

## Thermodynamics of the $\text{AlF}_3$ formation

We probed the thermodynamic possibility of the formation of  $\text{AlF}_3$  by comparing the chemical potential of Al ( $\mu_{\text{Al}}$ ) in  $\text{AlF}_3$  and  $\text{Ti}_3\text{AlC}_2$ . We found that, for any reasonable  $\mu_{\text{F}}$ , the inequality  $\mu_{\text{Al}}(\text{AlF}_3) < \mu_{\text{Al}}(\text{Ti}_3\text{AlC}_2)$  always hold, except at very high temperature ( $< 5000$  K). Therefore, below 5000 K, the formation of  $\text{AlF}_3$  is preferred over the  $\text{Ti}_3\text{AlC}_2$  (Figure S5).

## Gibbs free energy

The molar Gibbs free energy of the reaction  $\Delta G$  is defined as,

$$\Delta G = \sum \Delta G^{\text{products}} - \sum \Delta G^{\text{reactants}} \quad (\text{S2})$$

The Gibbs free energies of all the reactions were calculated using the following equation:

$$\Delta G = \Delta H - T\Delta S \quad (\text{S3})$$

where,  $\Delta H$  is the change in enthalpy,  $T$  is temperature and  $\Delta S$  is the entropy difference between the initial and final state. Here, the  $\Delta H$  are defined in terms of total energies of the species. The contribution due to entropy term  $T\Delta S$  is usually very small relative to  $\Delta H$ , [1] and here, except a rigid shift in  $\Delta H$  values, does not affect our conclusions.

Therefore, we have ignored the entropy contribution to Gibbs free energy. Precisely, the  $\Delta G$  of any reaction (here, explained for eq. 7 in main text) has been calculated as follows :

$$\Delta G = (E_{\text{Ti}_{12}\text{C}_8\text{F}_4} + 4E_{\text{AlF}_3} + 16\mu_{\text{H}} - E_{\text{Ti}_{12}\text{Al}_4\text{C}_8} + 16E_{\text{HF}}) \quad (\text{S4})$$

$\mu$ 's are the chemical potential of species participating in the reaction.

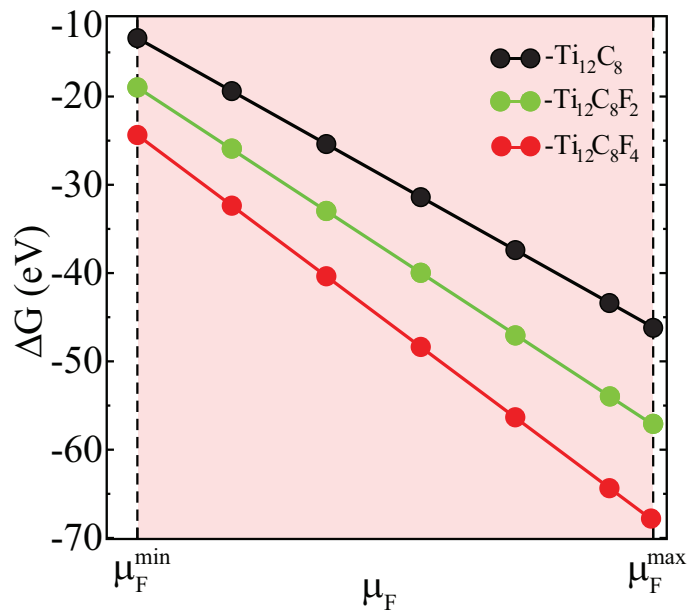


Figure S6: Change in the Gibbs free energy of reaction ( $\Delta G$ ) as function of hydrogen chemical potential, for different possible reaction path.

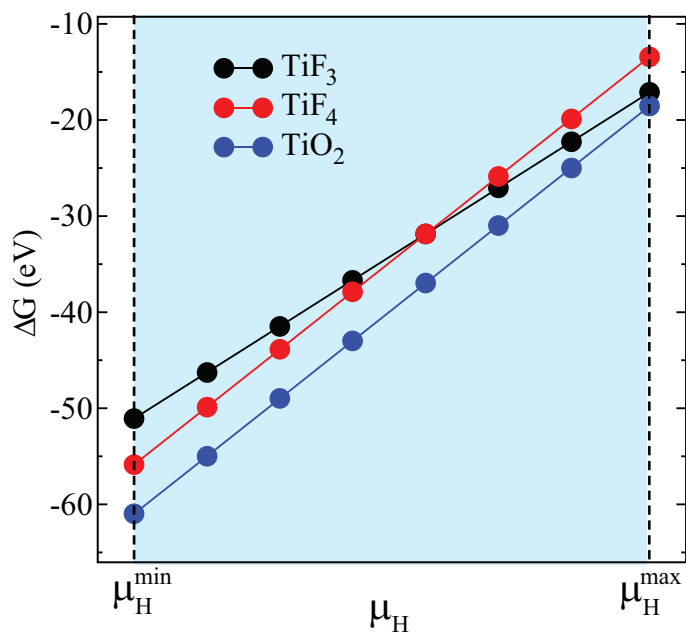


Figure S7: Change in the Gibbs free energy of reaction ( $\Delta G$ ) as a function of hydrogen chemical potential  $\mu_H$  for different possible reactions given as eq. 15-17 in main text.

## References

- [1] Ashton, M.; Mathew, K.; Hennig, R. G.; Sinnott, S. B. Predicted Surface Composition and Thermodynamic Stability of MXenes in Solution. *J. Phys. Chem. C* **2016**, *120*, 3550–3556