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Supporting Information:

Variation in interface strength of Silicon with surface engineered Ti_3C_2 MXenes

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Section I. Surface area (A) of $Ti_3C_2T_x$ MXene systems:

Work of separation is calculated from surface energies of materials. Therefore, our primary objective is to get the exact surface area of each MXene, which comes in contact with *a*-Si. The three monolayer MXene models considered in the study have functional groups attached to the surface under-coordinated Ti atoms above the hollow site between three neighboring C atoms. The structures are periodic in the x-y dimension and have a vacuum in z dimension. The vacuum of 20 Å is found optimum for -OH and -OH/O functionalized MXene systems, while energy of -F functionalized MXene converges with 30 Å vacuum. Table S1 summarizes the simulation cell dimensions of monolayer MXenes after DFT optimization. The presence of functional groups (-OH, -O, -F) modify Ti-C bond differently in individual MXene, resulting in very slight modifications of x-y (slightly by <=0.01Å for each MXene)[1]. Considering the orientation and dimensions of the surfaces in the study, surface area (A) has been calculated based on the formula described Figure S1 for each individual MXene interface system.

Table S1. Summary of simulation cell dimensions of monolayer MXenes after DFT optimization

MXene	**Box Dimensions after optimization**		
Terminations	**x (Å)**	**y (Å)**	**Area (Å^2)**
-OH	12.333	12.344	131.65
-OH/O	12.293	12.297	130.60
-F	12.286	12.272	130.81

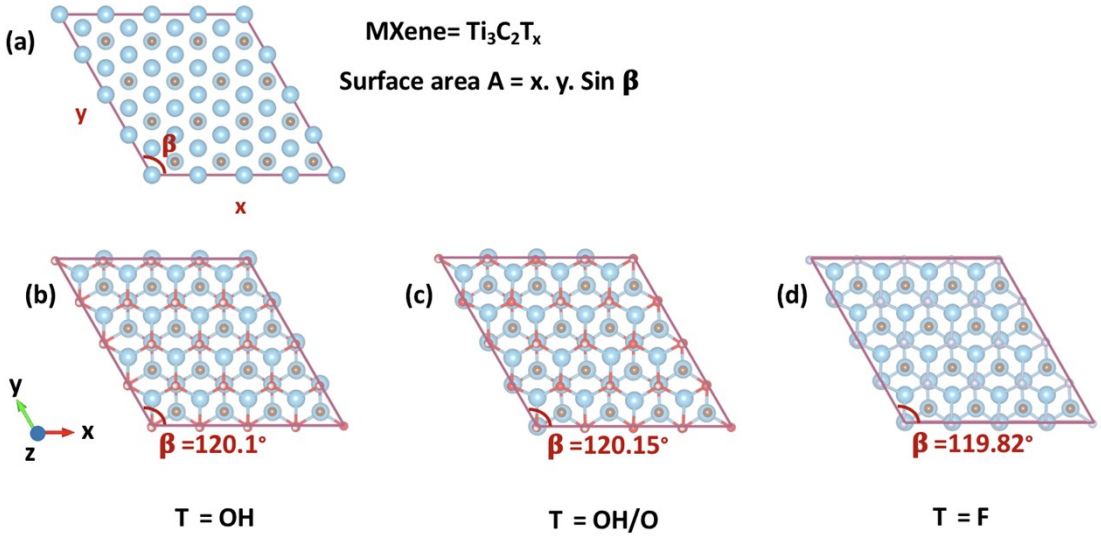

Figure S1. Top view of MXene surfaces in our study. These are representative of surfaces which come in contact with *a*-Si during interface formation. A = x.y.Sinβ is used for surface area determination.

Section II. Interface strength of *a*-Si/ $Ti_3C_2F_2$ interface with different interfacial gap *d* :

Interface system *a*-Si/ $Ti_3C_2F_2$ has the lowest interface strength (0.115 J/m^2) and highest interfacial net electron exchange (Δq) when the interfacial gap *d* is 2.14Å. This low interface strength is primarily on account of high concentration of charges and strained Ti-F bonds in the interfacial region, as demonstrated in Figure S2 (a1-a3). The interface strength of *a*-Si/ $Ti_3C_2F_2$ improved significantly when the interfacial gap *d* was expanded to 3.28Å. The W_{sep} value is calculated to be 0.335 J/m^2. The electron exchange (Δq) at the interface (determined by bader charge analysis) is very low. It suggests that the resultant interface is held by very weak vdW forces, as shown in Figure S2 (b1-b3). The interface also appears to be free of atomic strains. Table S2 compares both the interface systems. Physisorption appears as a primary bonding mechanism in the second interface (Table S2, *ii*), similar to *a*-Si/ $Ti_3C_2(OH)_2$ interface. Yet, the *a*-Si/ $Ti_3C_2(OH)_2$ interface has the highest interface strength (0.606 J/m^2) in the present study. The analysis highlights the dependence of interface strength on the interfacial gap and bonding mechanism at two materials' interface.

Table S2. Comparison of *a*-Si/ $Ti_3C_2F_2$ interface strength with varied interfacial gap *d*.

S. no.	**Functional Group**	**Interface strength (W_{sep})**	**Electrons exchanged (Δq)**	***d***
(i)	T = F	0.115 J/m^2	2.32 e^{-1}	2.14Å
(ii)	T = F	0.335 J/m^2	0.38 e^{-1}	3.28 Å

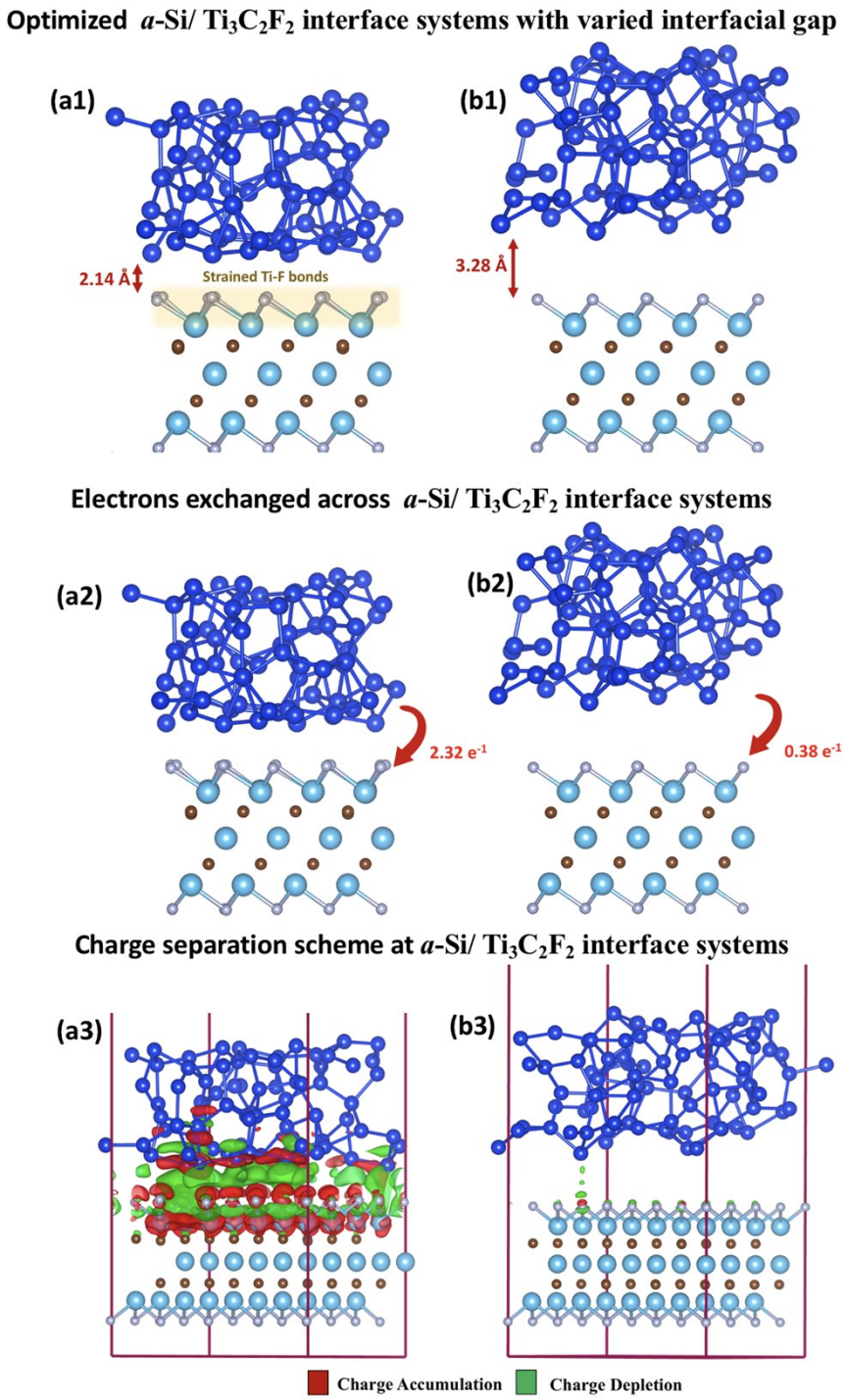

Figure S2. Comparison of *a*-Si/ $Ti_3C_2F_2$ interface systems with varied interfacial gap d. (a1-b1) Atomic representation of optimized *a*-Si/ $Ti_3C_2F_2$ interface systems with interfacial gap 2.14 Å and 3.28Å. (a2-b2) Atomic representation of *a*-Si/ $Ti_3C_2F_2$ systems depicting net electron transfer across the interface. (a3-b3) Charge separation scheme across the *a*-Si/ $Ti_3C_2F_2$ interface systems with red depicting charge accumulation and green representing charge depletion.

References

1. Tang, Q.; Zhou, Z.; Shen, P., Are MXenes promising anode materials for Li ion batteries? Computational studies on electronic properties and Li storage capability of Ti3C2 and Ti3C2X2 (X= F, OH) monolayer. *Journal of the American Chemical Society* **2012,** *134* (40), 16909-16916.