Electronic Supplemental Information for

Rational design of surface termination of $Ti_3C_2T_2$ MXenes for lithium-ion battery anodes

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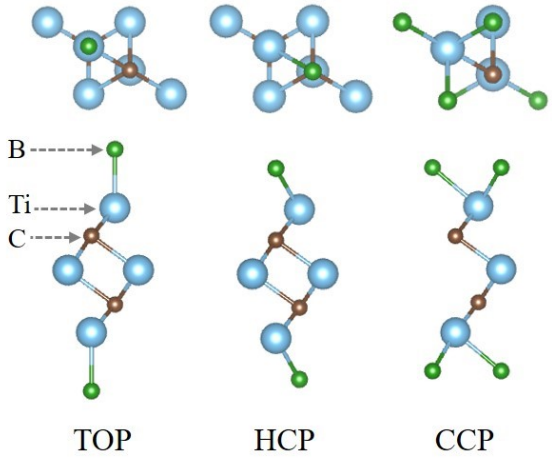

Fig. S1. Top and Side view of $Ti_3C_2B_2$.

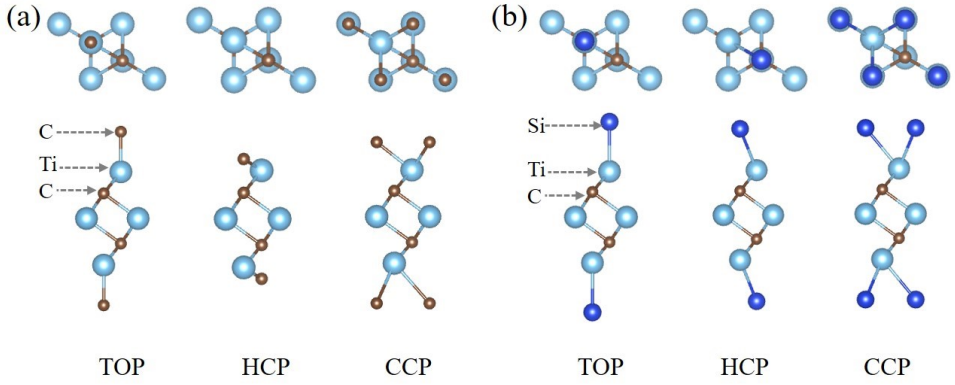

Fig. S2. Top and Side view of (a) Ti_3C_4 and (b) $Ti_3C_2Si_2$.

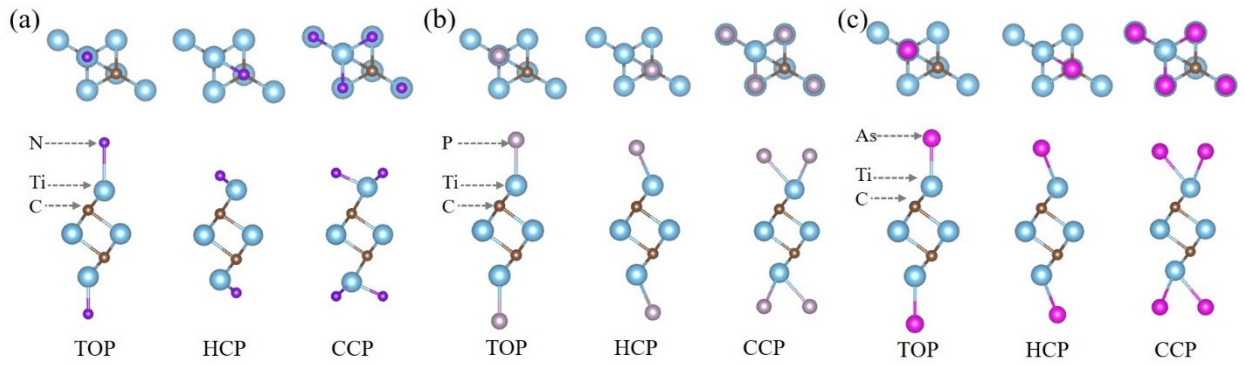

Fig. S3. Top and Side view of (a) $Ti_3C_2N_2$, (b) $Ti_3C_2P_2$ and (c) $Ti_3C_2As_2$.

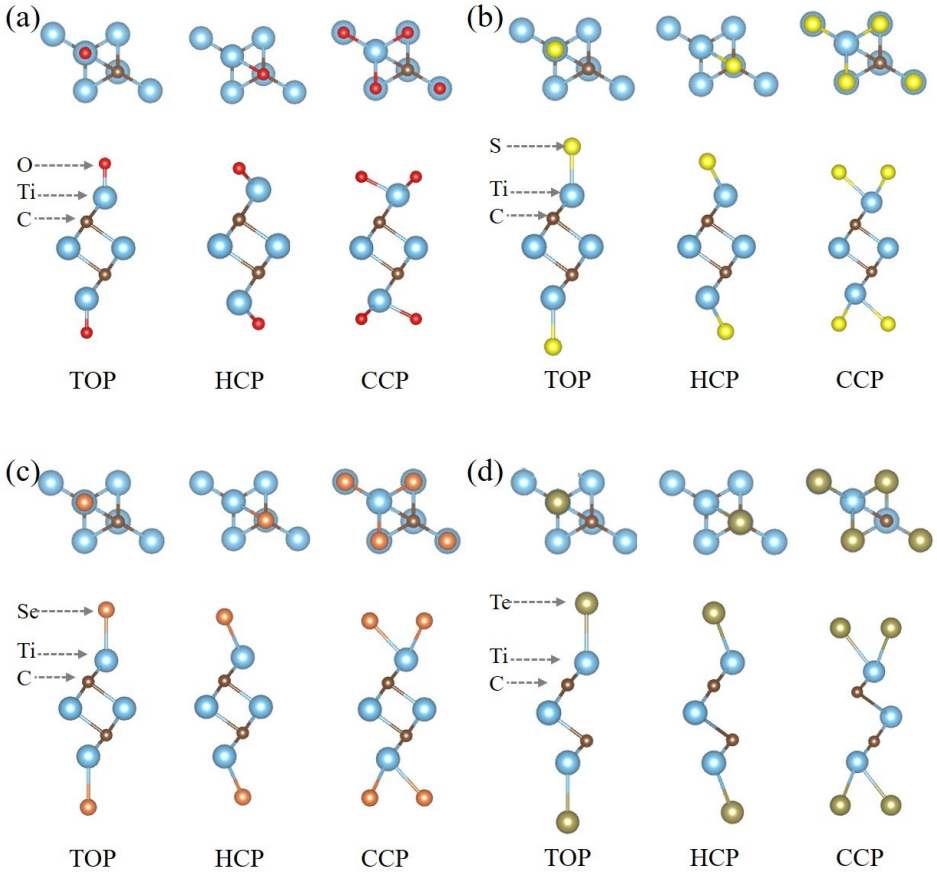

Fig. S4. Top and Side view of (a) $Ti_3C_2O_2$, (b) $Ti_3C_2S_2$, (c) $Ti_3C_2Se_2$ and (d) $Ti_3C_2Te_2$.

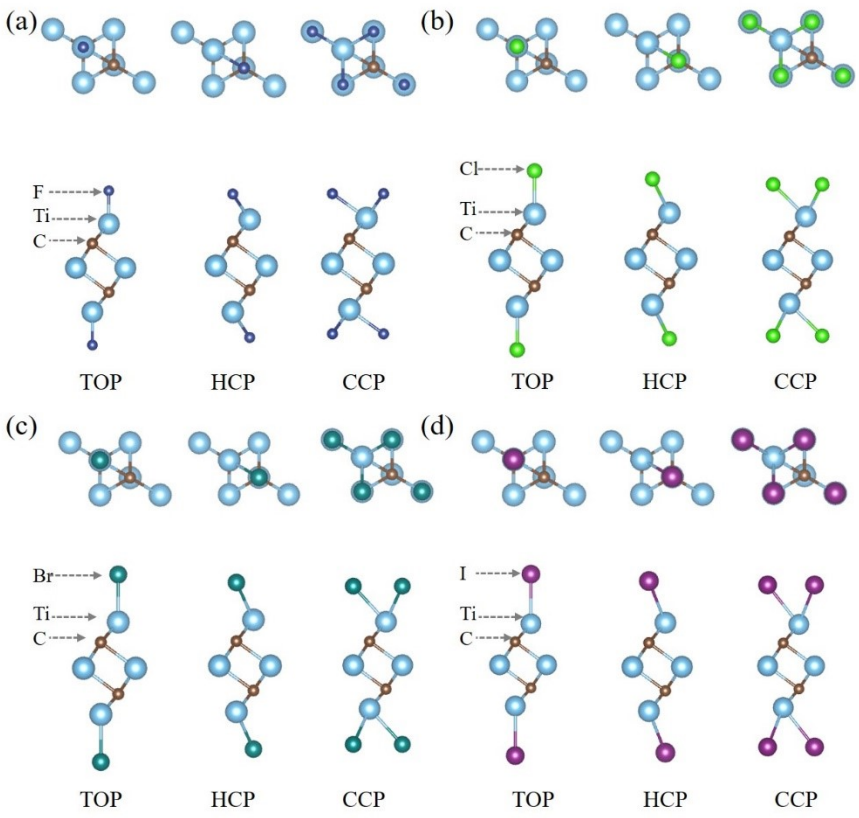

Fig. S5. Top and Side view of (a) $Ti_3C_2F_2$,(b) $Ti_3C_2Cl_2$, (c) $Ti_3C_2Br_2$ and (d) $Ti_3C_2I_2$.

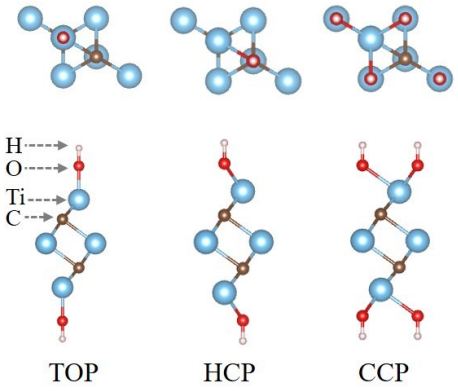

Fig. S6. Top and Side view of $Ti_3C_2(OH)_2$.

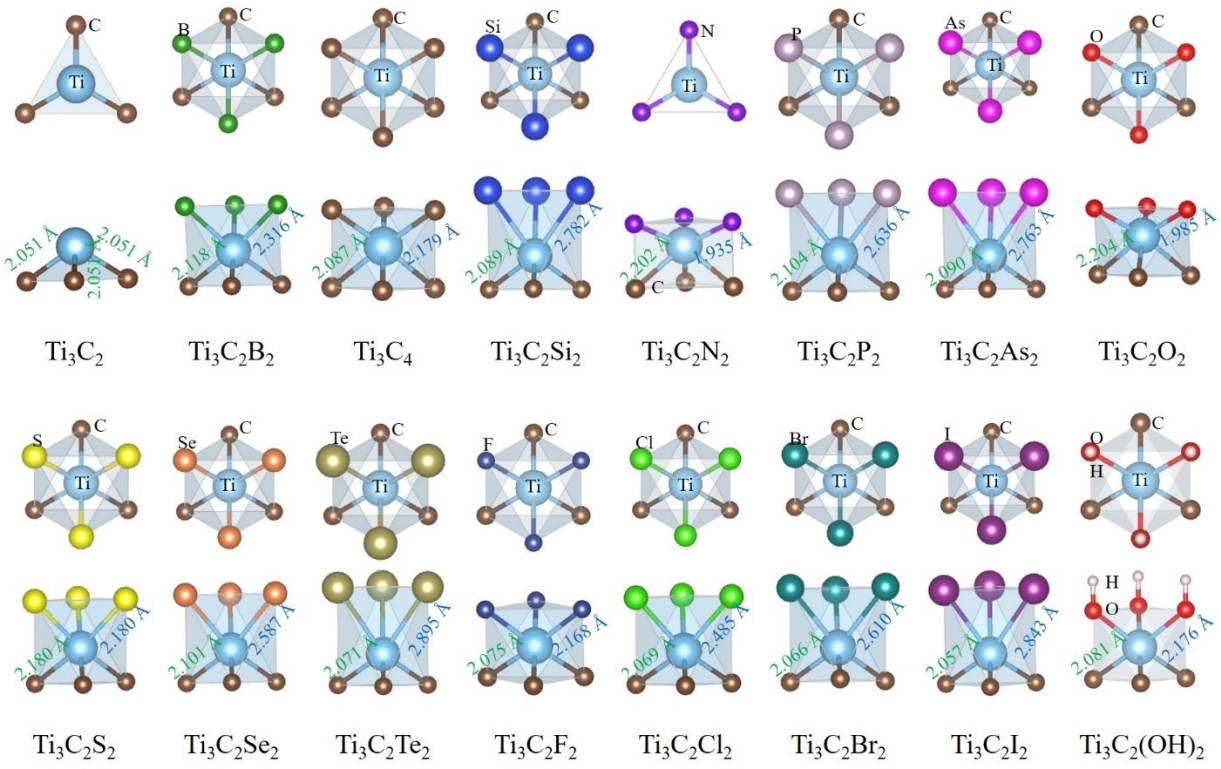

Fig. S7. The polyhedron structures, Ti-C and Ti-T bond length on the surface of $Ti_3C_2T_2$ from top and side views.

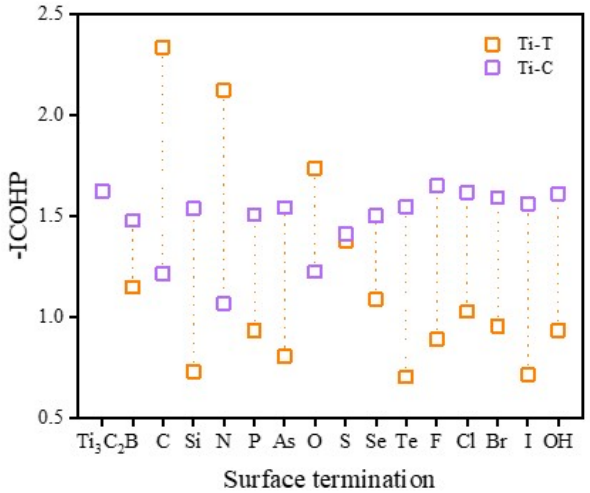

Fig. S8. The ICOHP of Ti-T bond and Ti-C bond in the surface polyhedron. ICOHP of Ti-T bond differs for different nonmetal and changes vary considerably. In contrast, ICOHP of Ti-C in the surface polyhedron remains small changes.

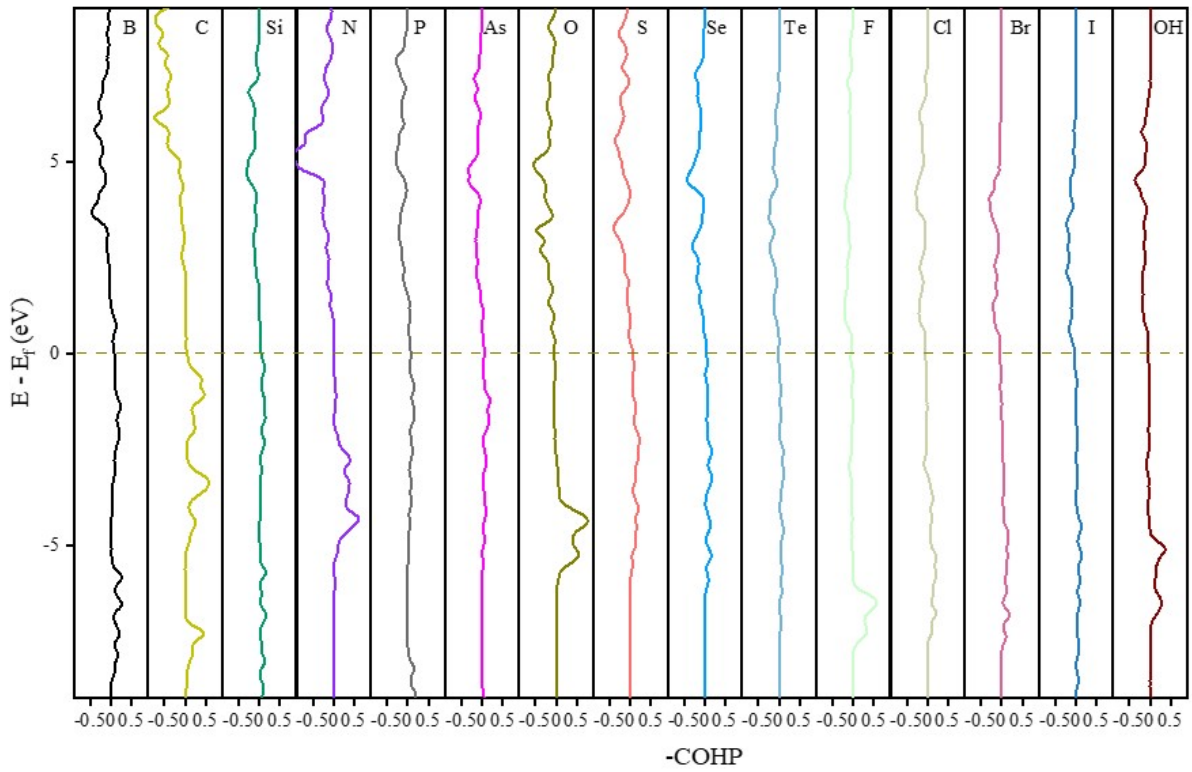

Fig. S9. COHP of Ti-T bond in the surface polyhedron.

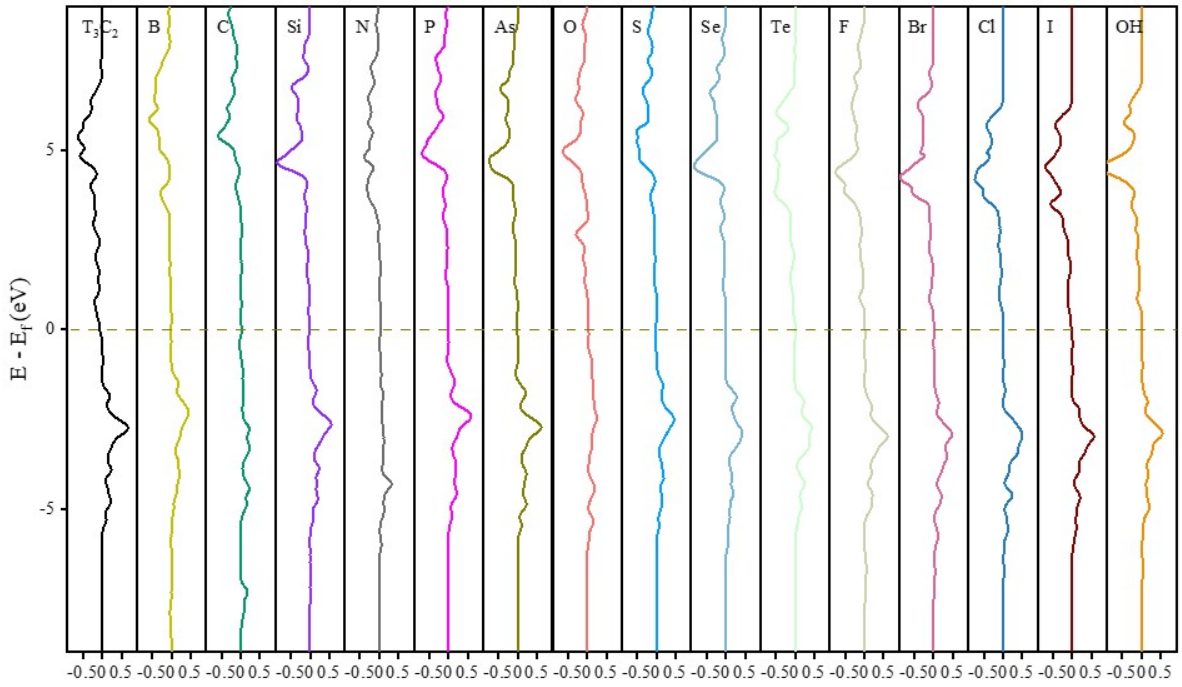

Fig. S10. COHP of Ti-C bond in the surface polyhedron.

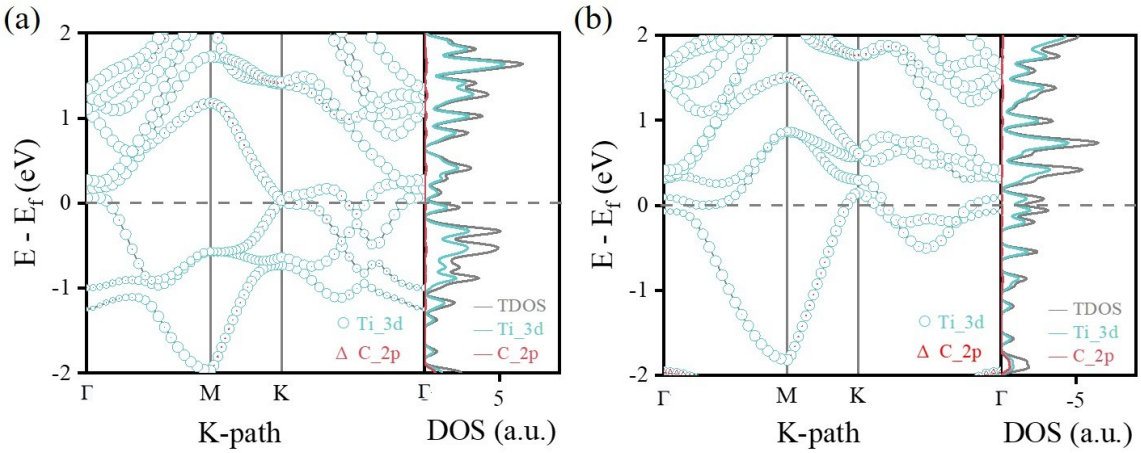

Fig. S11. (a) Spin-up and (b) spin-down electronic band structures and density of states (DOS) of Ti_3C_2.

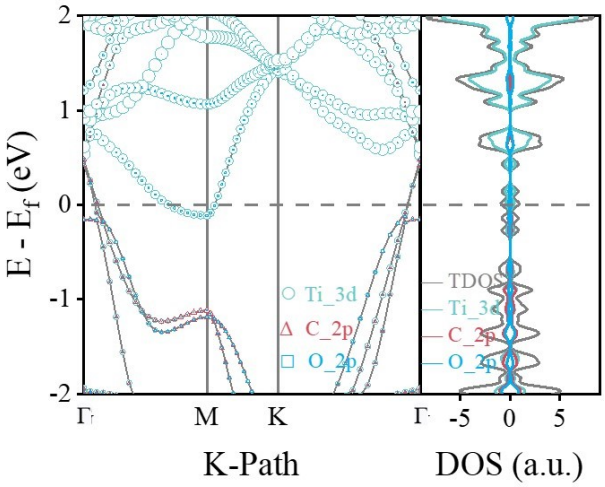

Fig. S12. Electronic band structure and DOS of $Ti_3C_2O_2$.

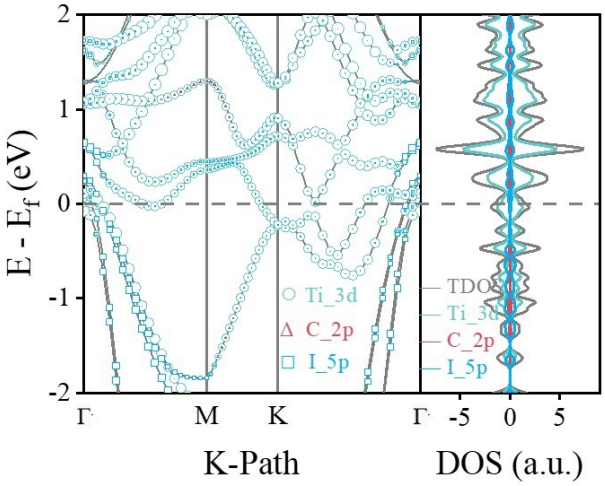

Fig. S13. Electronic band structure and DOS of $Ti_3C_2I_2$.

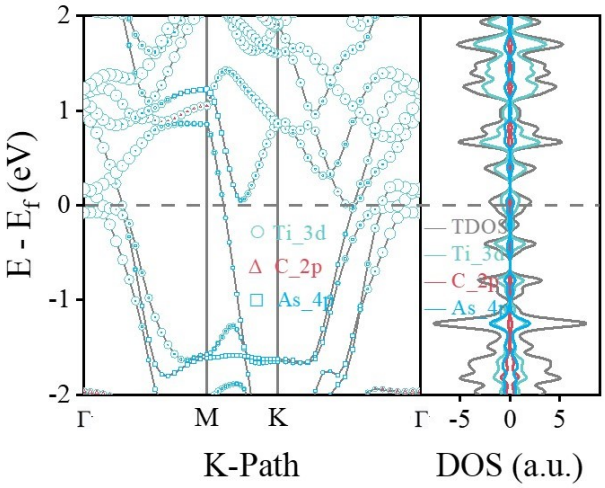

Fig. S14. Electronic band structure and DOS of $Ti_3C_2As_2$.

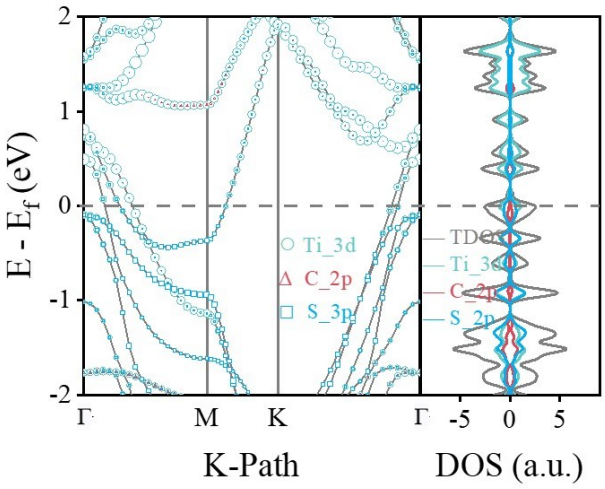

Fig. S15. Electronic band structure and DOS of $Ti_3C_2S_2$.

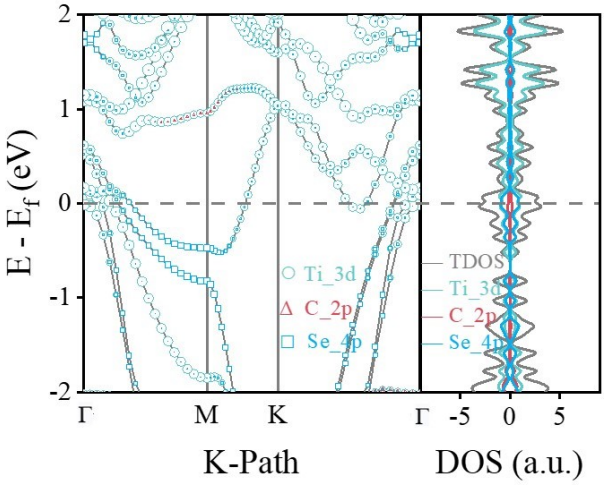

Fig. S16. Electronic band structure and DOS of $Ti_3C_2Se_2$.

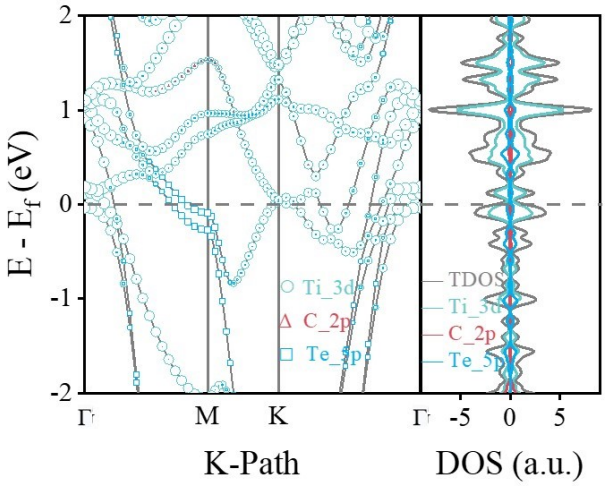

Fig. S17. Electronic band structure and DOS of $Ti_3C_2Te_2$.

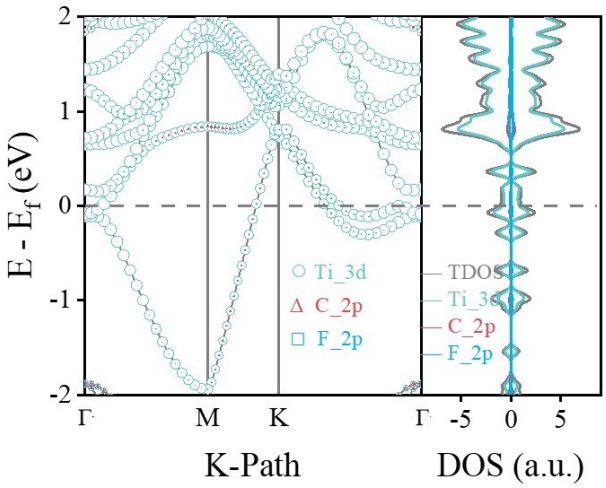

Fig. S18. Electronic band structure and DOS of $Ti_3C_2F_2$.

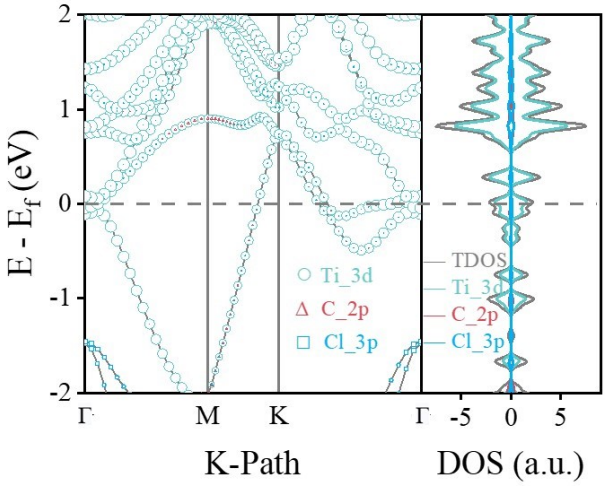

Fig. S19. Electronic band structure and DOS of $Ti_3C_2Cl_2$.

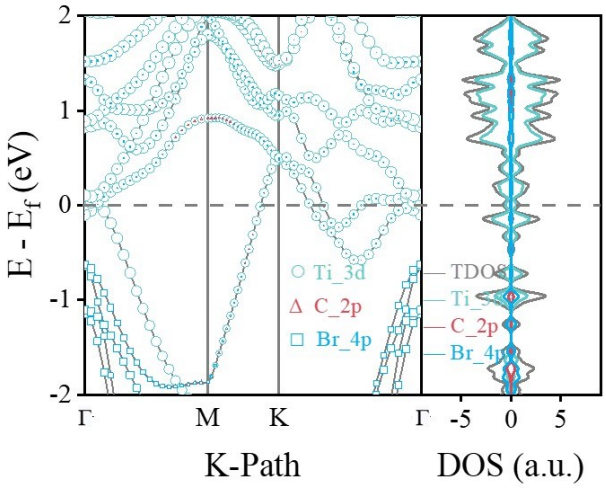

Fig. S20. Electronic band structure and DOS of $Ti_3C_2Br_2$.

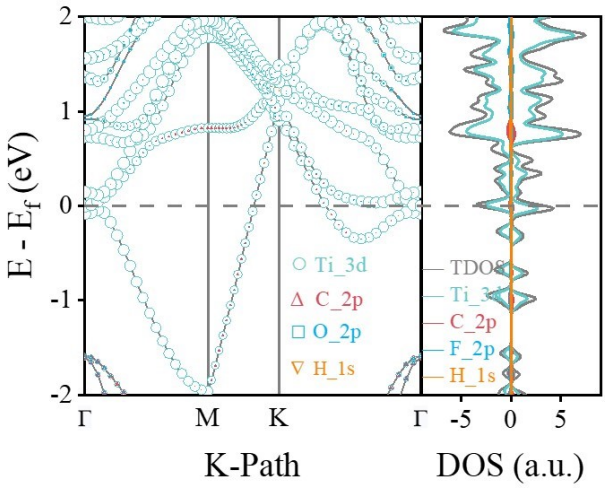

Fig. S21. Electronic band structure and DOS of $Ti_3C_2(OH)_2$.

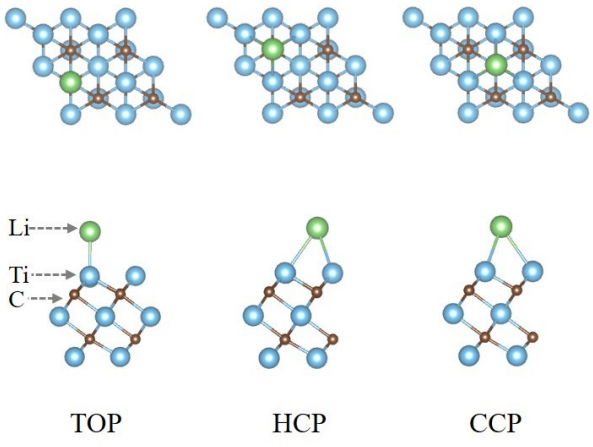

Fig. S22. Top and side views of Li-ion absorbed on Ti_3C_2.

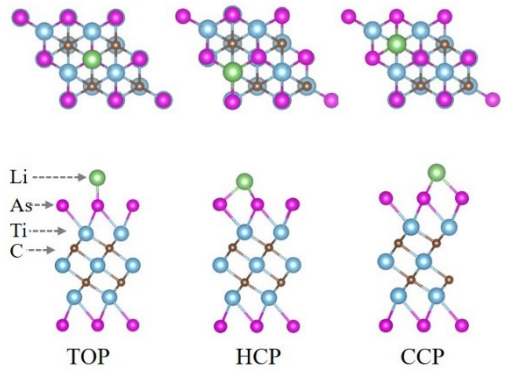

Fig. S23. Top and side views of Li-ion absorbed on $Ti_3C_2As_2$.

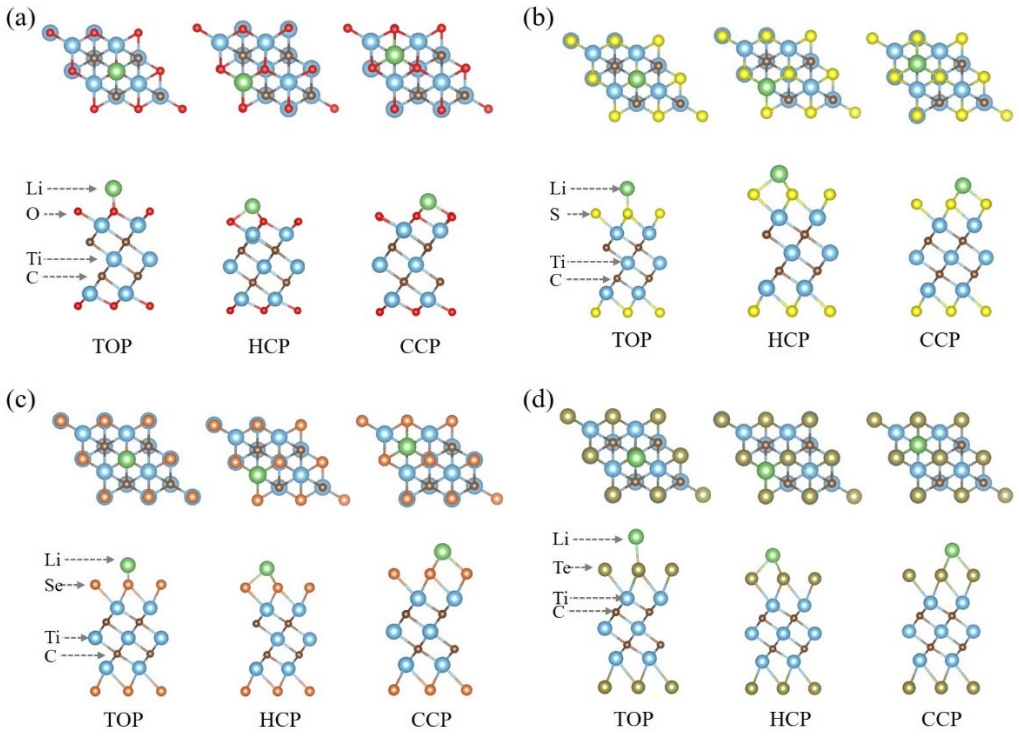

Fig. S24. Top and side views of Li-ion absorbed on $Ti_3C_2O_2$, $Ti_3C_2S_2$, $Ti_3C_2Se_2$ and $Ti_3C_2Te_2$.

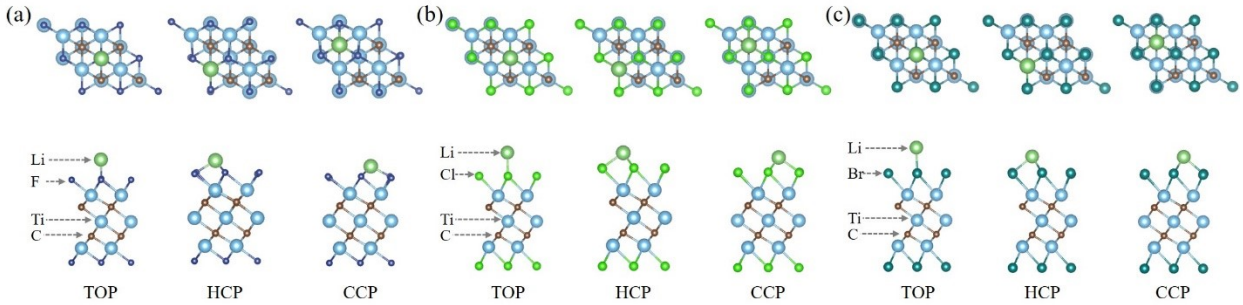

Fig. S25. Top and side views of Li-ion absorbed on $Ti_3C_2F_2$, $Ti_3C_2Cl_2$ and $Ti_3C_2Br_2$.

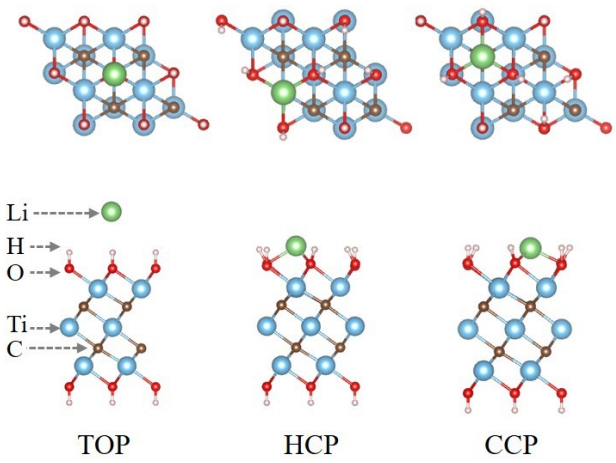

Fig. S26. Top and side views of Li-ion absorbed on $Ti_3C_2(OH)_2$.

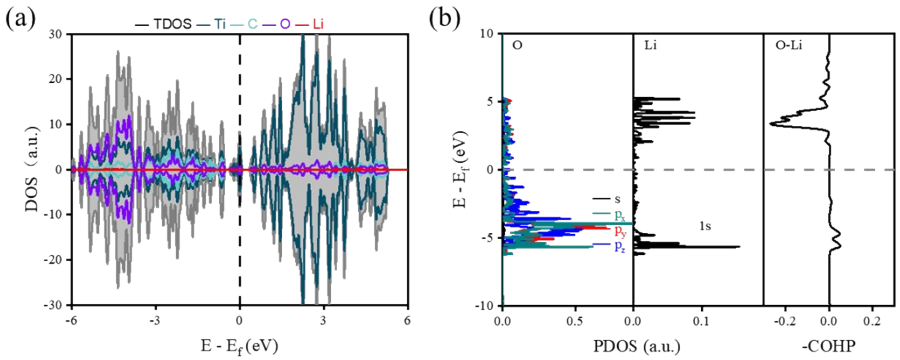

Fig. S27. (a) DOS of Li-ion absorded on $Ti_3C_2O_2$. (b) PDOS and COHP for O-Li bond.

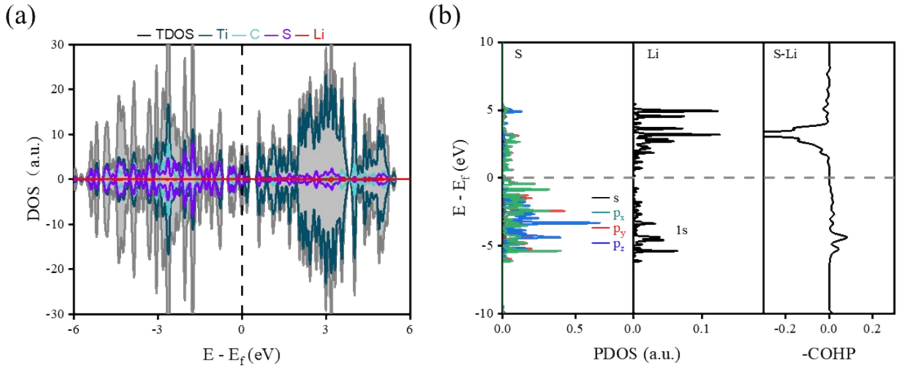

Fig. S28. (a) DOS of Li-ion absorded on $Ti_3C_2O_2$. (b) PDOS and COHP for S-Li bond.

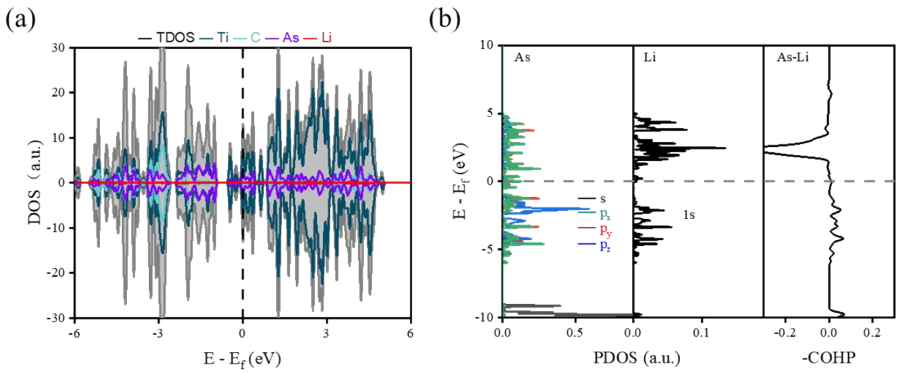

Fig. S29. (a) DOS of Li-ion absorded on $Ti_3C_2As_2$. (b) PDOS and COHP for As-Li bond.

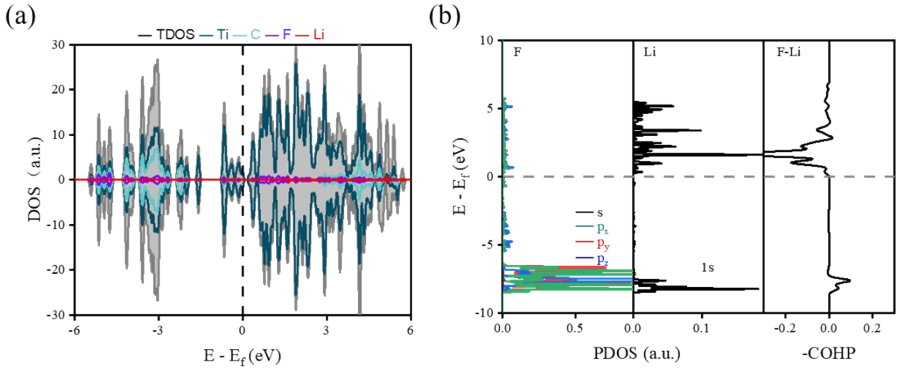

Fig. S30. (a) DOS of Li-ion absorded on $Ti_3C_2F_2$. (b) PDOS and COHP for F-Li bond.

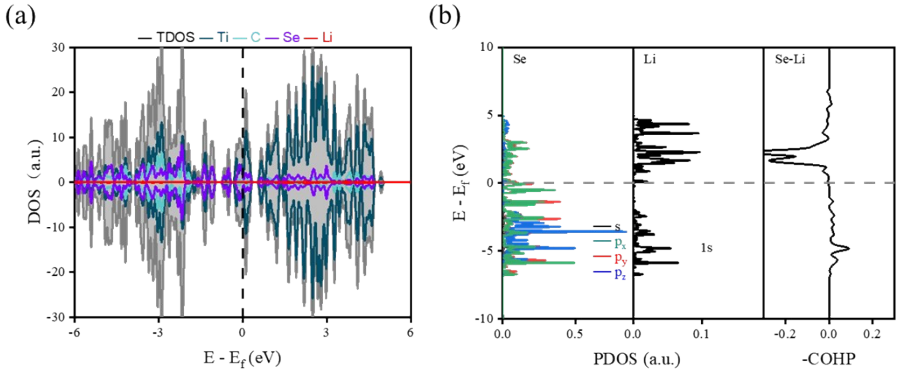

Fig. S31. (a) DOS of Li-ion absorded on $Ti_3C_2Se_2$. (b) PDOS and COHP for Se-Li bond.

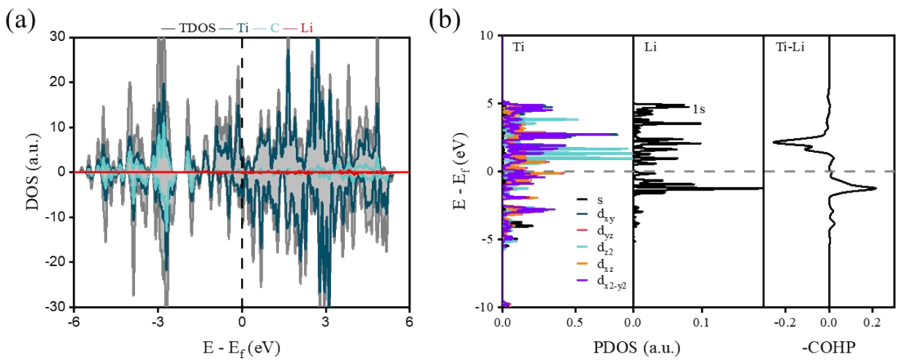

Fig. S32. (a) DOS of Li-ion absorded on Ti_3C_2. (b) PDOS and COHP for Ti-Li bond.

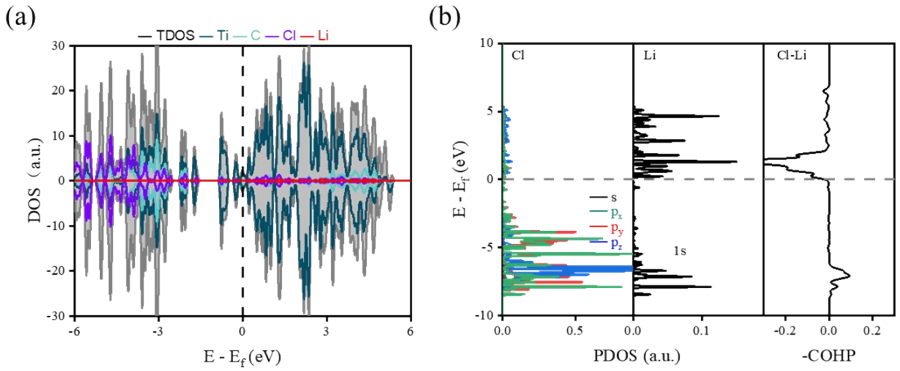

Fig. S33. (a) DOS of Li-ion absorded on $Ti_3C_2Cl_2$. (b) PDOS and COHP for Cl-Li bond.

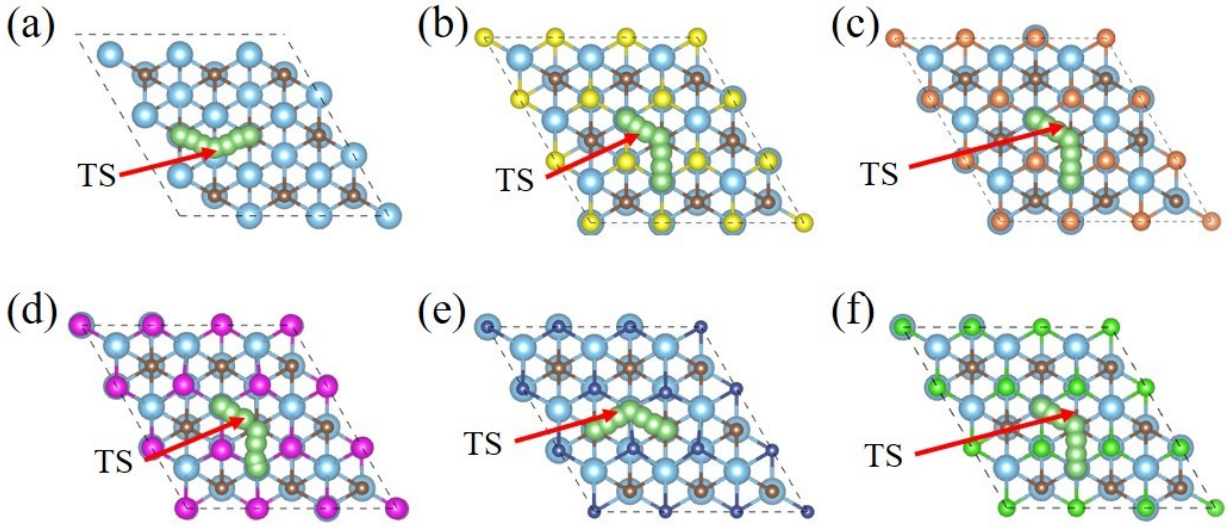

Fig. S34. Li-ion diffusion pathways for (a) Ti_3C_2, (b) $Ti_3C_2S_2$, (c) $Ti_3C_2Se_2$, (d) $Ti_3C_2As_2$, (e) $Ti_3C_2F_2$, and (f) $Ti_3C_2Cl_2$.

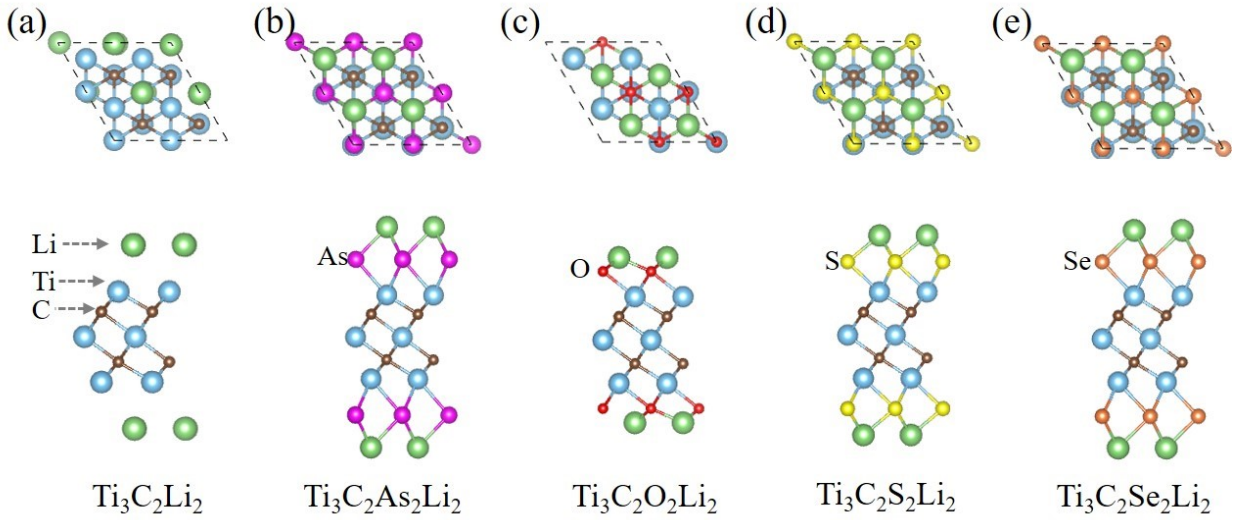

Fig. S35. One layer Li-ions adsorbed on (a) Ti_3C_2, (b) $Ti_3C_2As_2$, (c) $Ti_3C_2O_2$, (d) $Ti_3C_2S_2$ and (e) $Ti_3C_2Se_2$.

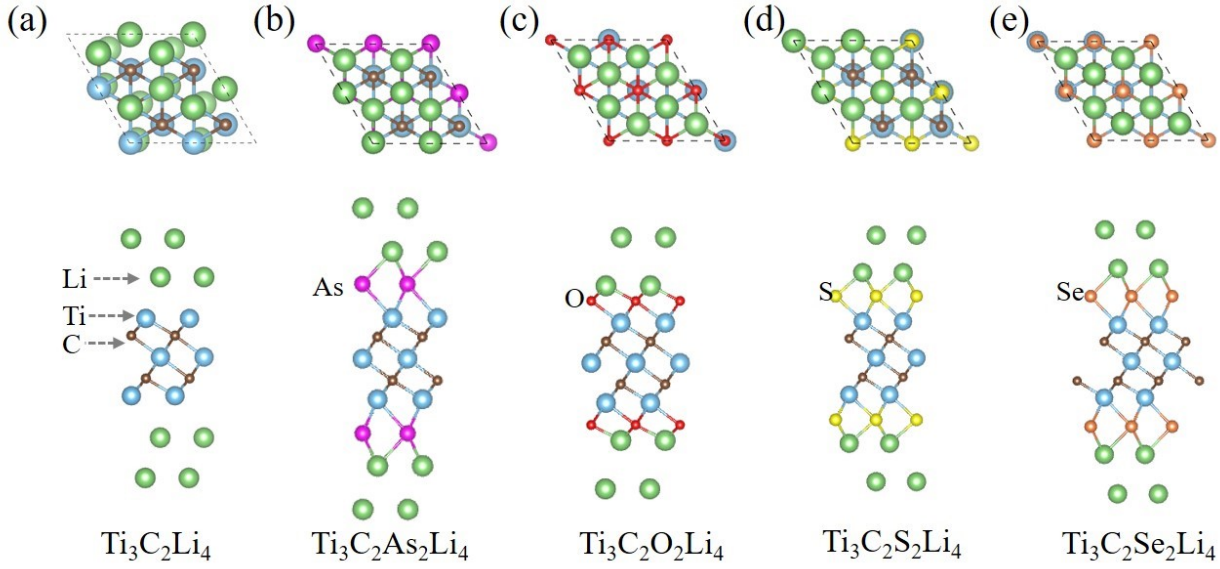

Fig. S36. Two layers Li-ions adsorbed on (a) Ti_3C_2, (b) $Ti_3C_2As_2$, (c) $Ti_3C_2O_2$, (d) $Ti_3C_2S_2$ and (e) $Ti_3C_2Se_2$.

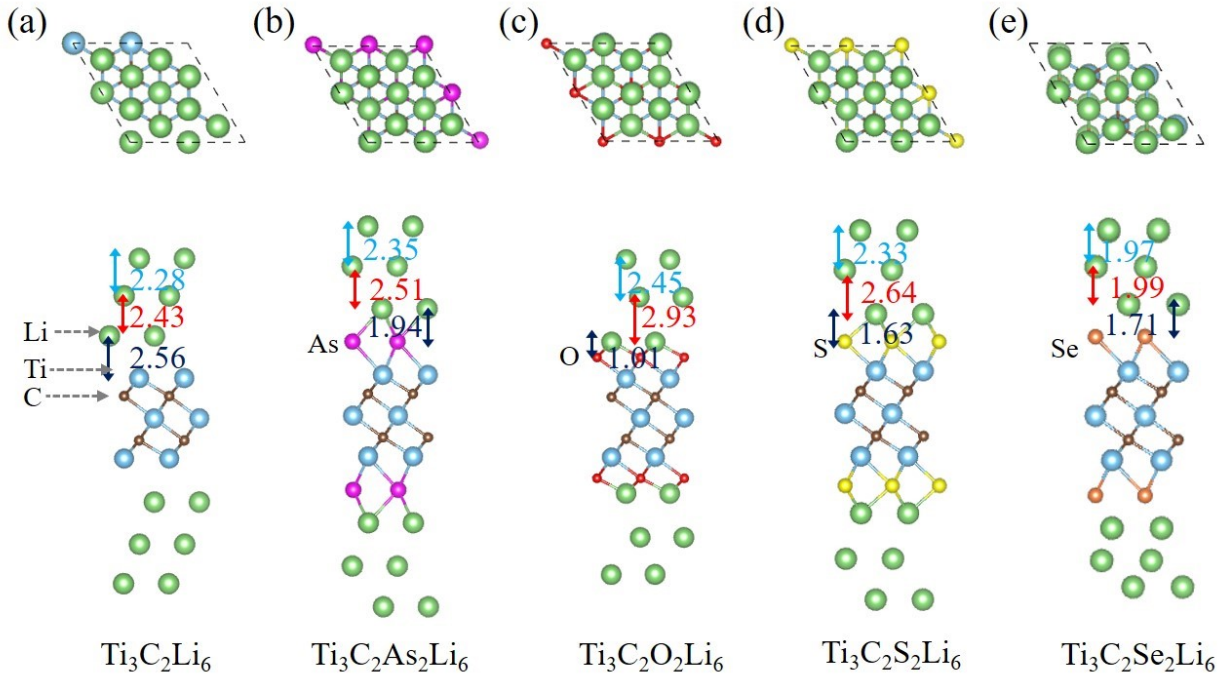

Fig. S37. Three layers Li-ions adsorbed on (a) Ti_3C_2, (b) $Ti_3C_2As_2$, (c) $Ti_3C_2O_2$, (d) $Ti_3C_2S_2$, (e) $Ti_3C_2Se_2$.

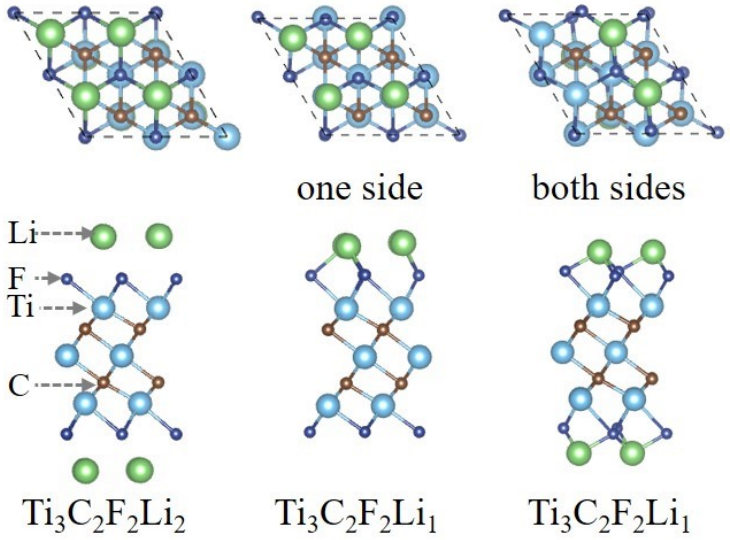

Fig. S38. Three different structure for Li-ions adsorbed on$Ti_3C_2F_2$. The sturcture of $Ti_3C_2F_2Li$ with both sides Li-ions adsorption was adopted for the lower nagetive energy. The adsorption energy for $Ti_3C_2F_2Li_2$ is positive (+0.67 eV).

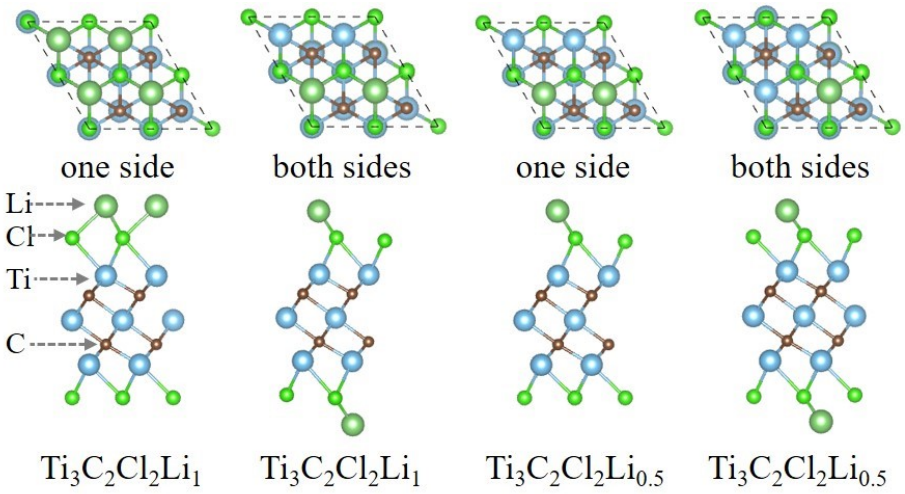

Fig. S39. Different structure for Li-ions adsorbed on$Ti_3C_2Cl_2$. The adsorption energy for $Ti_3C_2Cl_2Li_{0.5}$ with both sides Li-ion adsorption is nagetive, while others are positive.

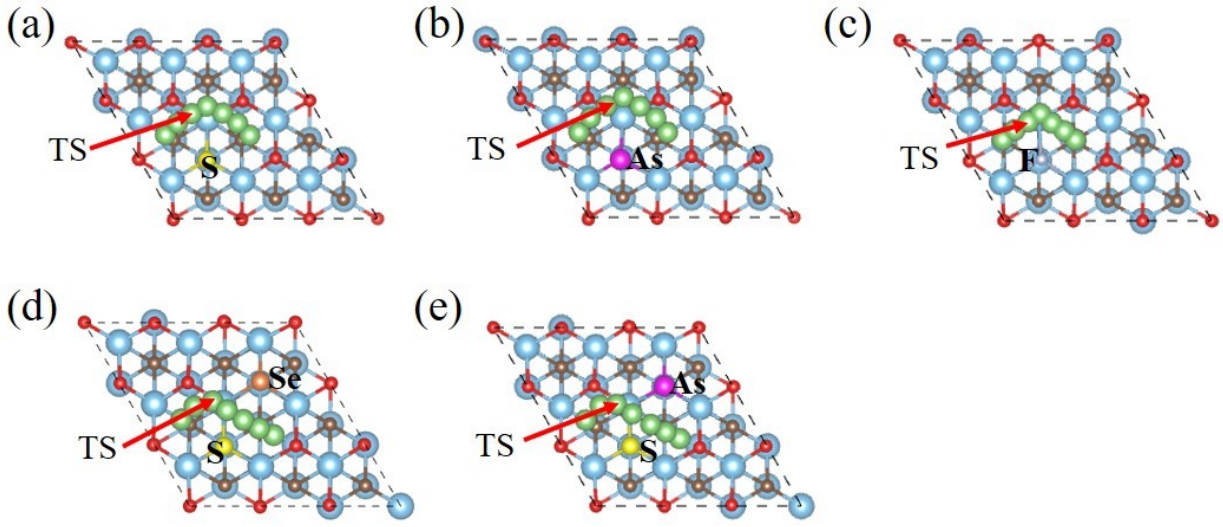

Fig. S40. Li-ion diffusiong pathways on $Ti_3C_2O_2$ with (a) S, (b) As, (c) F, (d) S and Se, (e) S and As doping.

Table S1 The Ti-C and Ti-T (functional groups) bonds in the surface polyhedron.

	Ti-T (T = functional nonmetal) bond (Å) in the surface polyhedron						Average bond length Å	Distortion index
	Ti-C1	Ti-C2	Ti-C3	Ti-T1	Ti-T2	Ti-T3		
Ti_3C_2	2.05148	2.05148	2.05148	/	/	/	2.0515	0
$Ti_3C_2B_2$	2.1181	2.11814	2.11819	2.31615	2.31631	2.31638	2.2172	0.04468
Ti_3C_4	2.08667	2.08733	2.08753	2.17859	2.17941	2.17957	2.1332	0.02157
$Ti_3C_2Si_2$	2.08948	2.08948	2.08948	2.78165	2.78165	2.78165	2.4356	0.1421
$Ti_3C_2N_2$	2.20199	2.20199	2.20199	1.93477	1.93477	1.93477	2.0684	0.0646
$Ti_3C_2P_2$	2.10457	2.10457	2.10457	2.63611	2.63611	2.63611	2.3703	0.11212
$Ti_3C_2As_2$	2.09048	2.09048	2.09048	2.76246	2.76246	2.76246	2.4265	0.13847
$Ti_3C_2O_2$	2.20465	2.20465	2.20465	1.98483	1.98483	1.98483	2.0947	0.05247
$Ti_3C_2S_2$	2.18003	2.18003	2.18003	2.18052	2.18052	2.18052	2.1803	0.00011
$Ti_3C_2Se_2$	2.10137	2.10137	2.10137	2.58689	2.58689	2.58689	2.3441	0.10356
$Ti_3C_2Te_2$	2.07137	2.07137	2.07137	2.89463	2.89463	2.89463	2.4832	0.16583
$Ti_3C_2F_2$	2.07504	2.07504	2.07504	2.16819	2.16819	2.16825	2.1216	0.02195
$Ti_3C_2Cl_2$	2.06852	2.06852	2.06852	2.48521	2.48521	2.48521	2.2769	0.09151
$Ti_3C_2Br_2$	2.06635	2.06635	2.06635	2.6102	2.6102	2.6102	2.3383	0.11629
$Ti_3C_2I_2$	2.05699	2.05699	2.05699	2.84263	2.84263	2.84263	2.4498	0.16035
$Ti_3C_2(OH)_2$	2.08064	2.08066	2.08066	2.17577	2.17577	2.17582	2.1282	0.02235

Table S2. The specific capacity for S, Se, F, Cl, S-Se and S-As doped $Ti_3C_2O_2$.

	Specific capacity (mAh/g)		
doping element	one layer	two layers	three layers
Without	268.50	537.01	805.51
S	267.31	534.62	801.92
Se	263.88	527.76	791.64
As	264.17	528.34	792.51
F	268.28	536.56	804.84
S-Se	262.72	525.45	788.17
S-As	263.01	526.03	789.04