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Surface potential-determined performance of $Ti_3C_2T_2$ (T=O, F, OH) and $Zr_3C_2T_2$ (T=O, F, OH, S) MXenes as anode materials of sodium ion batteries

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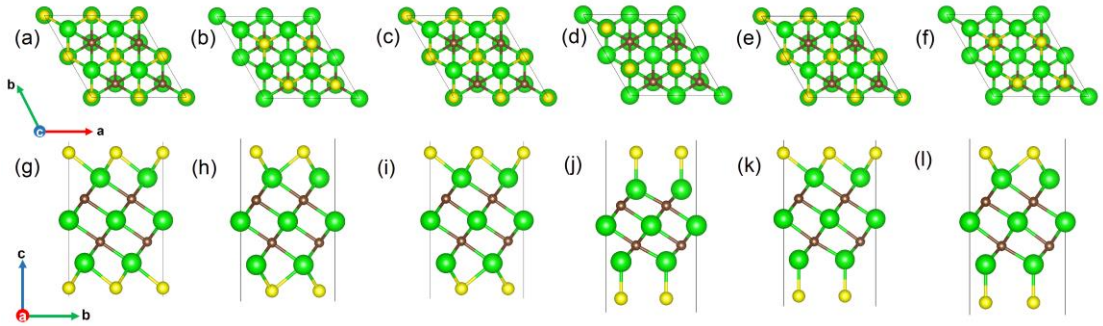

Fig. S1. Top- and side-views of six different models for $Zr_3C_2S_2$: (a) Model 1, with S on top-sites of middle zirconium atoms on both sides; (b) Model 2, with S on the top-sites of neighbouring carbon atoms on both sides; (c) Model 3, with S on the top-sites of middle zirconium atoms on one side, and on the top-sites of neighbouring carbon atoms on the other side; (d) Model 4, with S on the top-sites of neighbouring zirconium atoms on both sides; (e) Model 5, with S on the top-sites of middle zirconium atoms on one side, and on neighbouring zirconium atoms on the opposite side; (f) Model 6, with S on the top-sites of neighbouring carbon atoms on one side, and on the top-sides of neighbouring zirconium atoms on the other side. (g)-(l) corresponding side-views of the six models.

Table S1. Relative total energies ΔE (in eV) of Models 1-6 for $Zr_3C_2S_2$ based on their unit cells.

Models	**1**	2	3	4	5	6
ΔE	**0.000**	0.954	0.486	0.0303	2.25	2.65

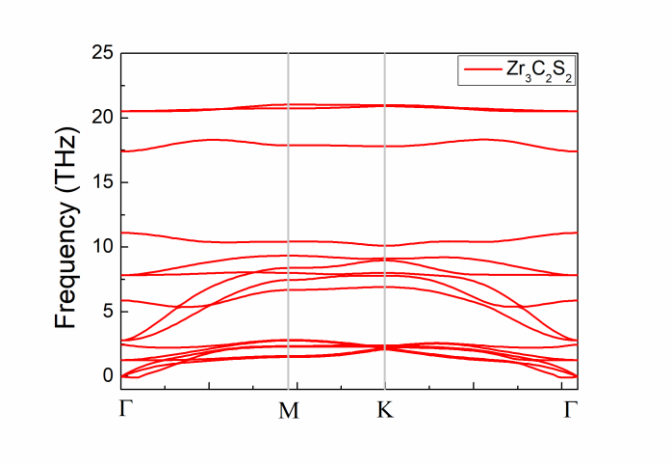

Fig. S2. Phonon dispersion of $Zr_3C_2S_2$.

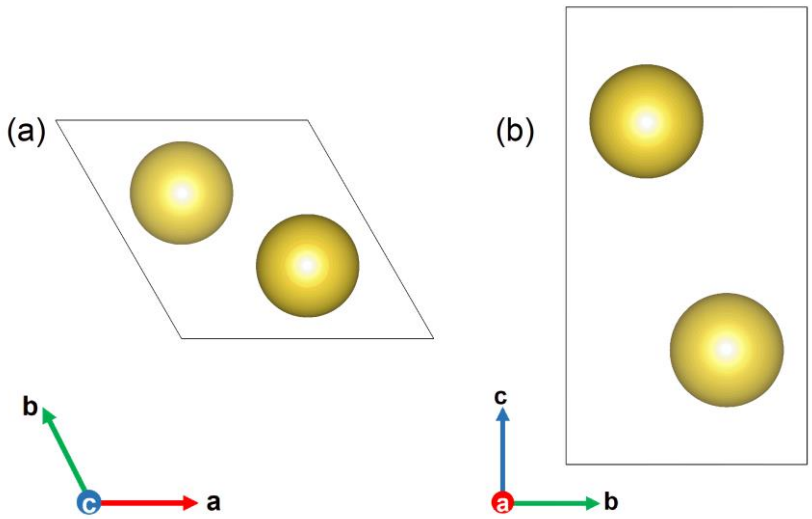

Fig. S3. Bulk sodium structure: (a) top-view; (b) side-view.

Table S2. The lattice parameters and energy per atom E_{atom} in bulk sodium.

Bulk Sodium	a (Å)	c (Å)	E_{atom} (eV)
PBE	3.730	6.124	-1.313
PBE+VDW	3.726	6.119	-1.463

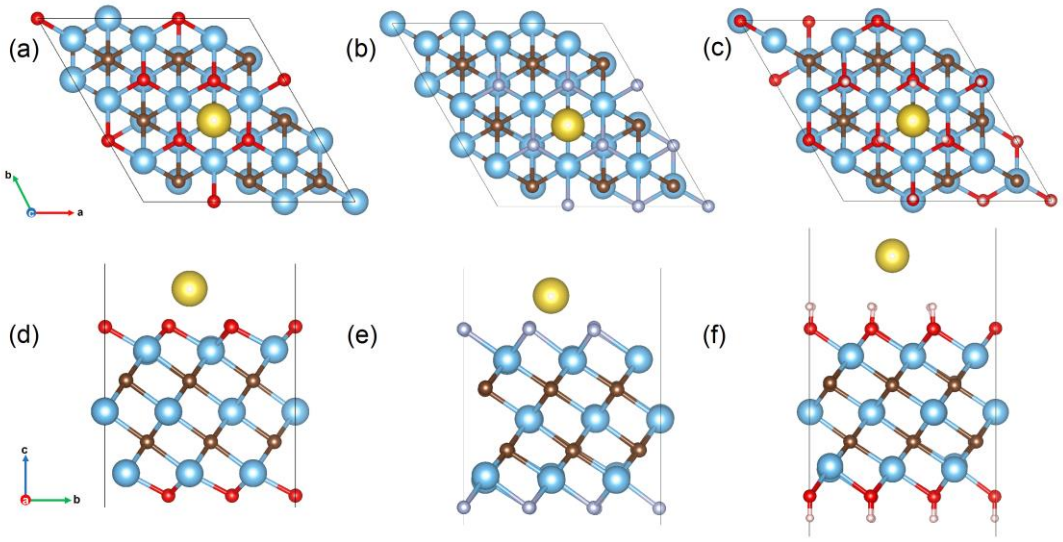

Fig. S4. Based on 3×3×1 supercells and from PBE+VDW+U, (a)-(c) show the $Ti_3C_2O_2$, $Ti_3C_2F_2$ and $Ti_3C_2(OH)_2$ structures of adsorbing a sodium atom, respectively. (d)-(e) show corresponding side-views.

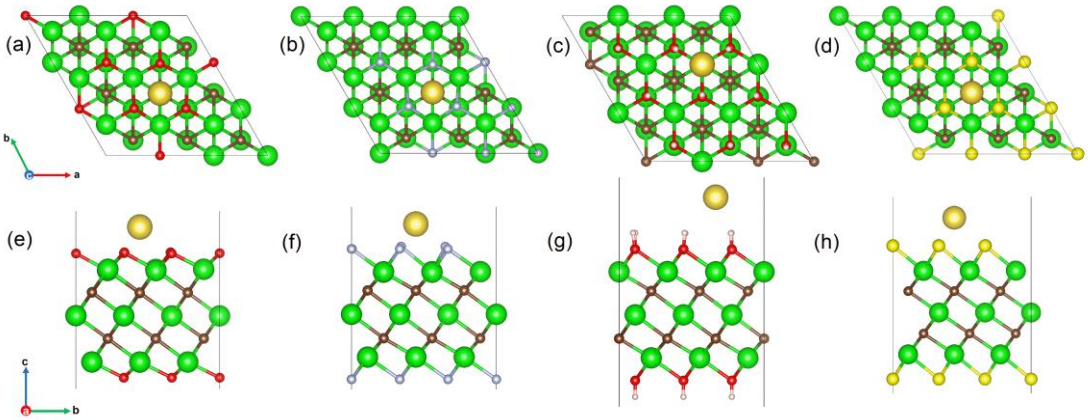

Fig. S5. Based on 3×3×1 supercells and from PBE+VDW+U, (a)-(d) show the $Zr_3C_2O_2$, $Zr_3C_2F_2$, $Zr_3C_2(OH)_2$ and $Zr_3C_2S_2$ structures of adsorbing a sodium atom, respectively. (e)-(h) show corresponding side-views.

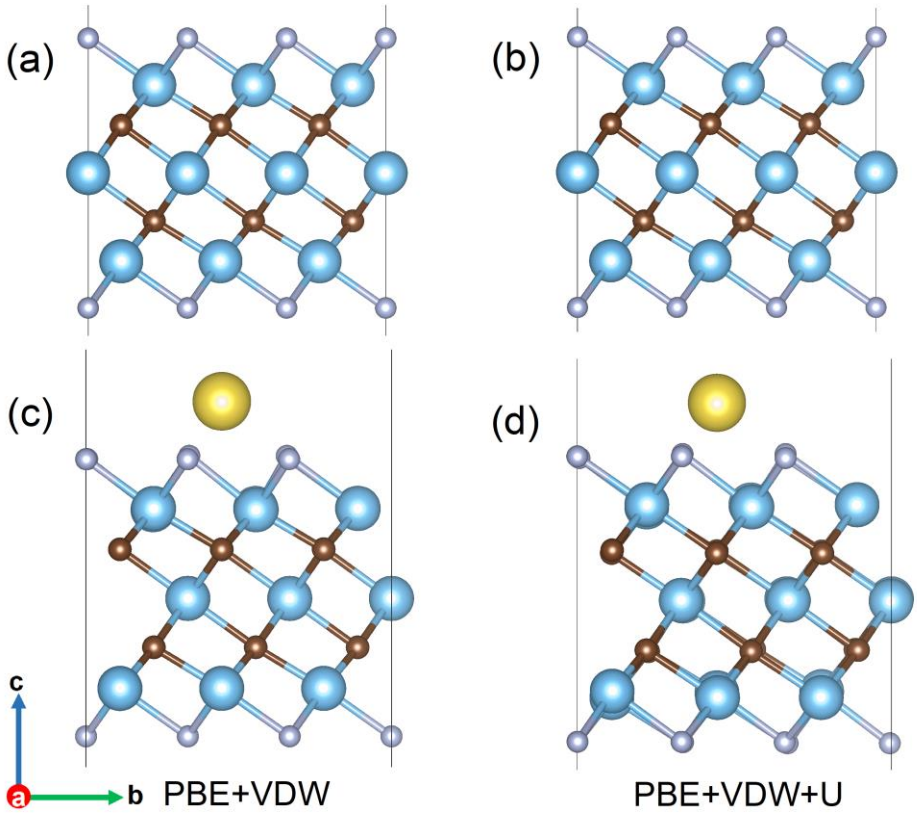

Fig. S6. (a) and (b) are the 3×3×1 supercells of $Ti_3C_2F_2$ from PBE+VDW and PBE+VDW+U, respectively. (c) and (d) are the corresponding $Ti_3C_2F_2$ supercells of adsorbing a sodium atom.

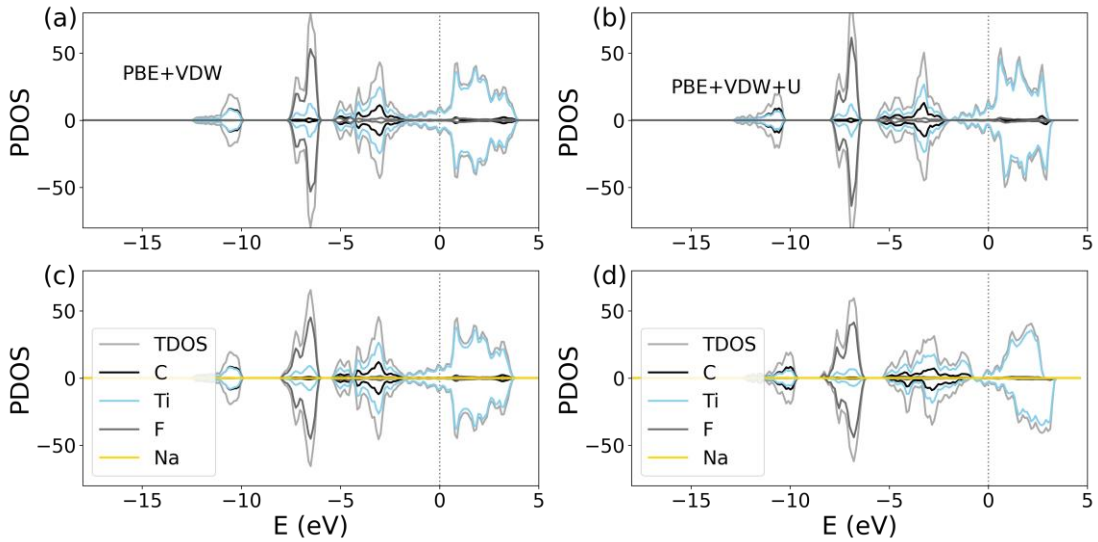

Fig. S7. (a) and (b) are the densities of states (DOSs) of 3×3×1 supercell $Ti_3C_2F_2$ from PBE+VDW and PBE+VDW+U, respectively. (c) and (d) are the DOSs of 3×3×1 supercell $Ti_3C_2F_2$ of adsorbing a sodium atom, from PBE+VDW and PBE+VDW+U, respectively.

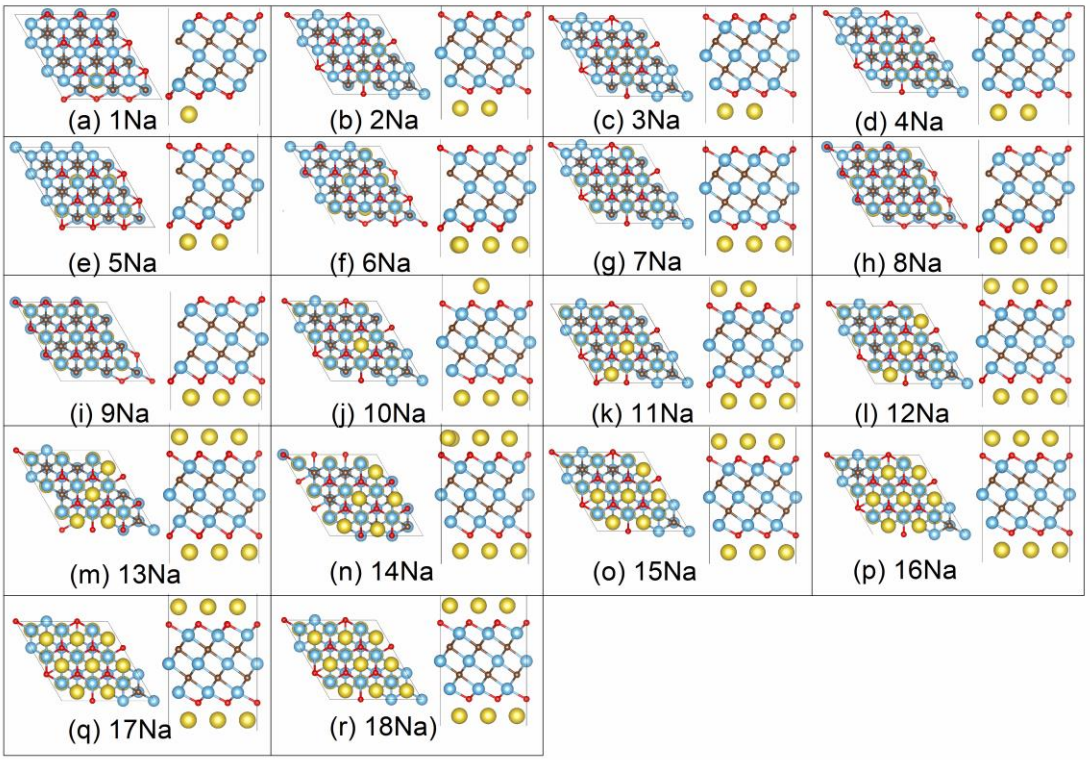

Fig. S8. Based on the 3×3×1 supercell of $Ti_3C_2O_2$, the number of adsorbed sodium atoms increases from one to eighteen; the sodium atoms firstly occupy one side, and then stabilize on the other side.

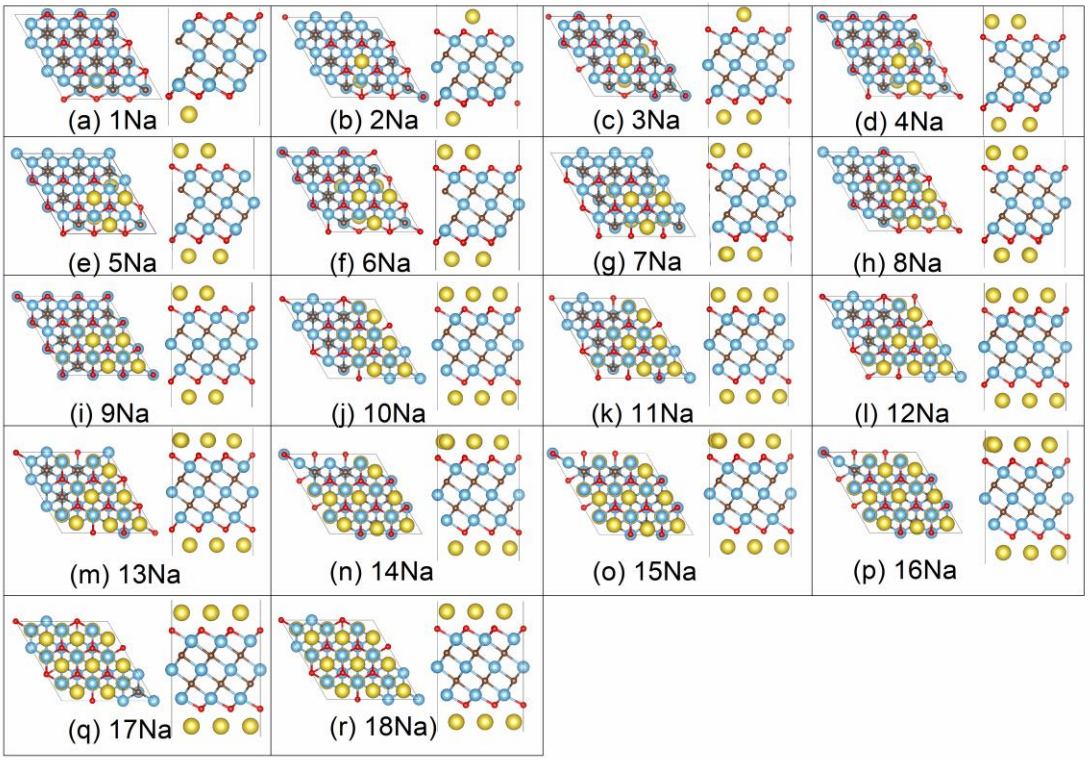

Fig. S9. Based on the 3×3×1 supercell of $Ti_3C_2O_2$, the number of adsorbed sodium atoms increases from one to eighteen. The sodium atoms occupy two sides

simultaneously.

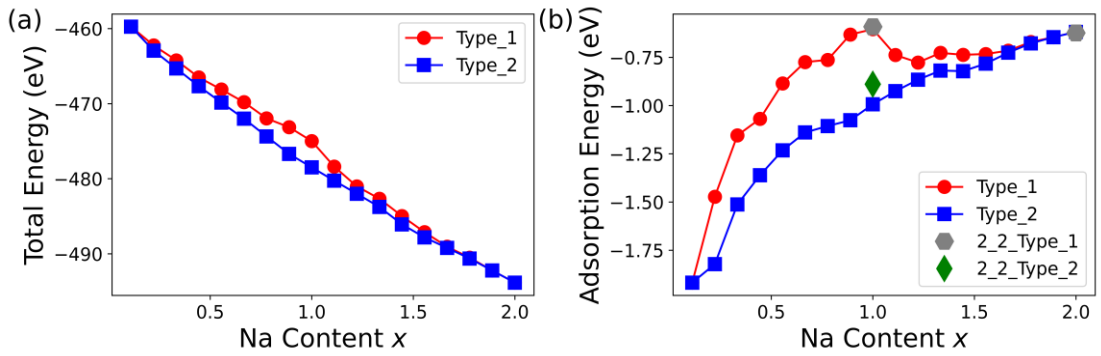

Fig. S10. (a) Total energies of 3×3×1 supercell $Ti_3C_2O_2$ with increasing numbers of adsorbed sodium atoms from PBE+VDW+U. The red circles show the total energies of the structures shown in Figure S3, which are denoted as Type_1. The blue squares show the total energies of the structures presented in Figure S4, which are denoted as Type_2; (b) corresponding adsorption energies for Type_1 and Type_2 structures. The grey hexagons and green diamonds present corresponding adsorption energies of sodium based on the 2×2×1 supercells of $Ti_3C_2O_2$.

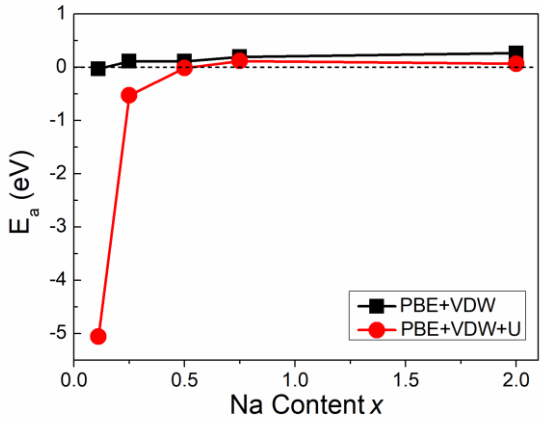

Fig. S11. Adsorption energy of sodium on $Ti_3C_2(OH)_2$ based on PBE+VDW and PBE+VDW+U.

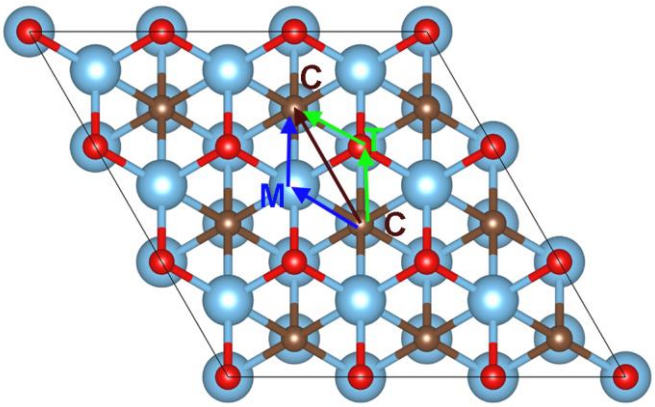

Fig. S12. Three possible migration paths for sodium on $M_3C_2T_2$ MXenes. The brown arrow shows that sodium migrates from a C-site to its neighbouring C-site directly. The blue arrow presents the route that sodium takes from a C-site moveing to a neighbouring M-site, before migrating to another neighbouring C-site. The green arrow shows the path along which sodium moves from a C-site to a neighbouring T-site, and then migrates to another neighbouring C-site.

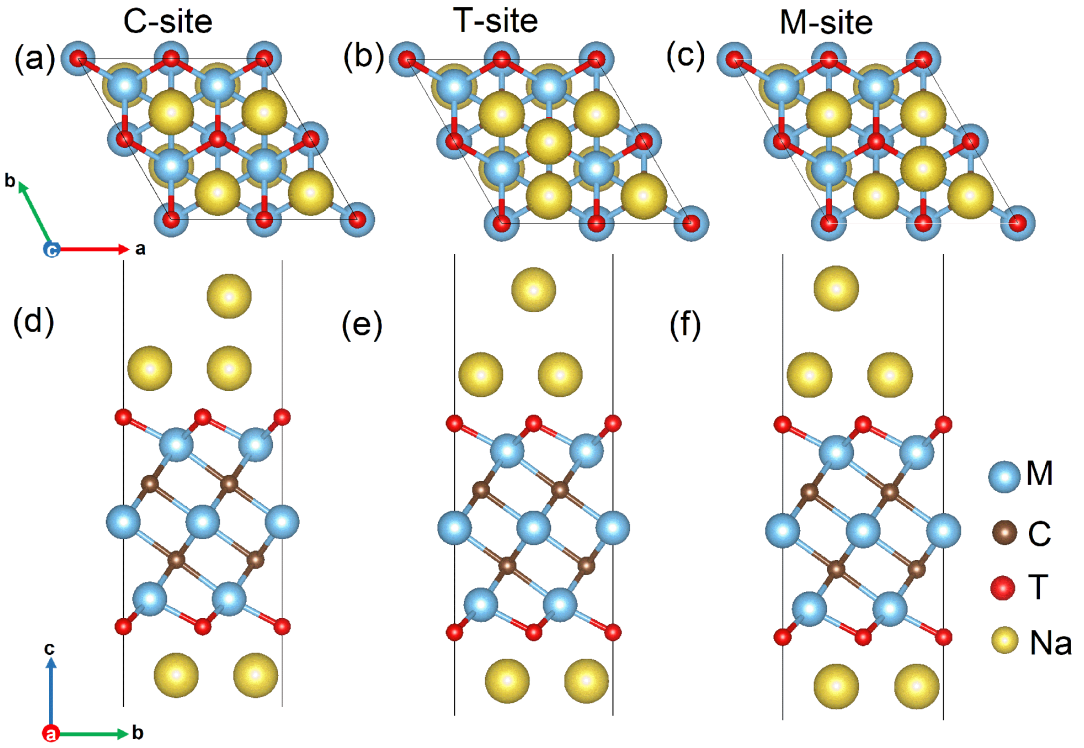

Fig. S13. Possible adsorption sites for the second layer of sodium atoms: (a) the sodium atom is on the top-site of neighbouring carbon, and this configuration is also denoted as C-site; (b) the sodium atom is on the top-site of neighbouring T, and this structure is denoted as T-site. (c) the sodium atom is on the top-site of neighbouring M atom, and the configuration is denoted as M-site. (d)-(f) corresponding side-views of the structures in (a)-(c).

Table S3. Adsorption energies (in eV) for one sodium in the second layer on the 2×2×1 supercell of $M_3C_2T_2$ MXenes based on PBE+VDW+U.

Configurations	C-site	T-site	M-site
$Ti_3C_2O_2$	-0.173	**-0.176**	-0.174
$Ti_3C_2F_2$	0.326	**0.208**	0.234
$Zr_3C_2O_2$	0.465	**-0.143**	-0.140
$Zr_3C_2S_2$	0.00175	**-0.0391**	-0.0385

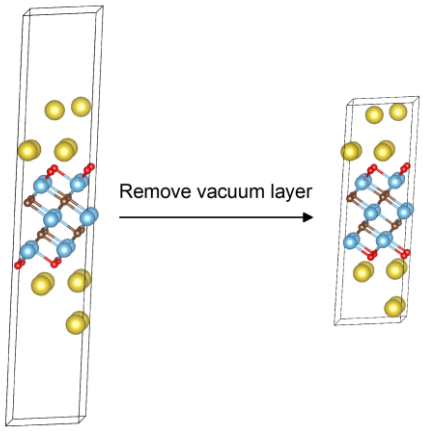

Fig. S14. Schematic diagram of the removal of the vacuum layer of 2D $Ti_3C_2O_2Na_3$ to build a bulk state.

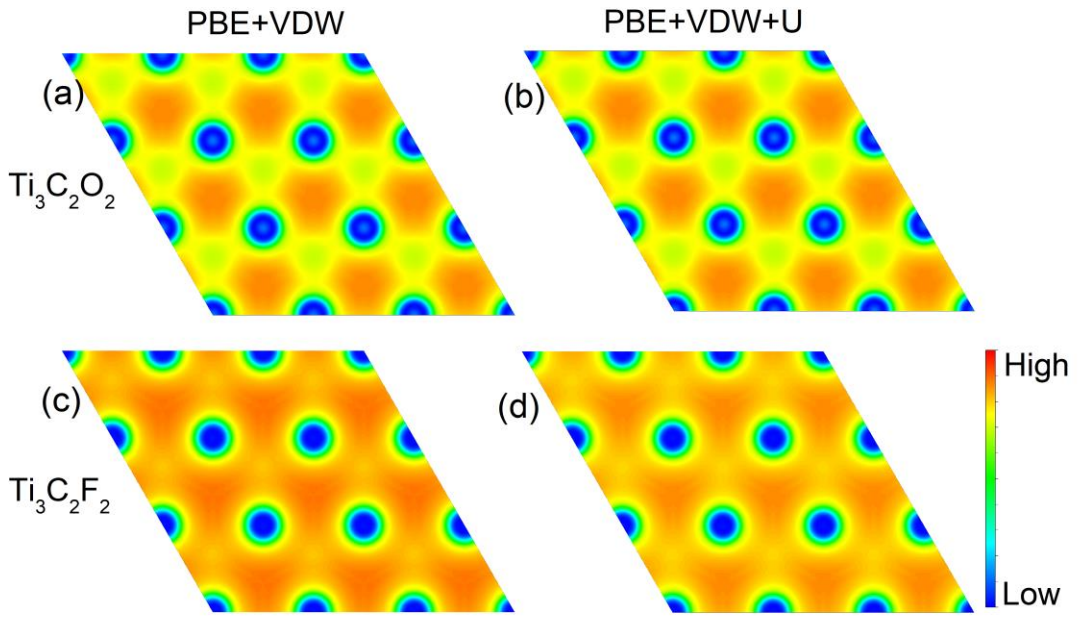

Fig. S15. (a) and (b) Two-dimensional (2D) potential diagrams at the surfaces of $Ti_3C_2O_2$ from PBE+VDW and PBE+VDW+U, respectively; (c) and (d) 2D potential diagrams at the surfaces of $Ti_3C_2F_2$ from the two functionals above.

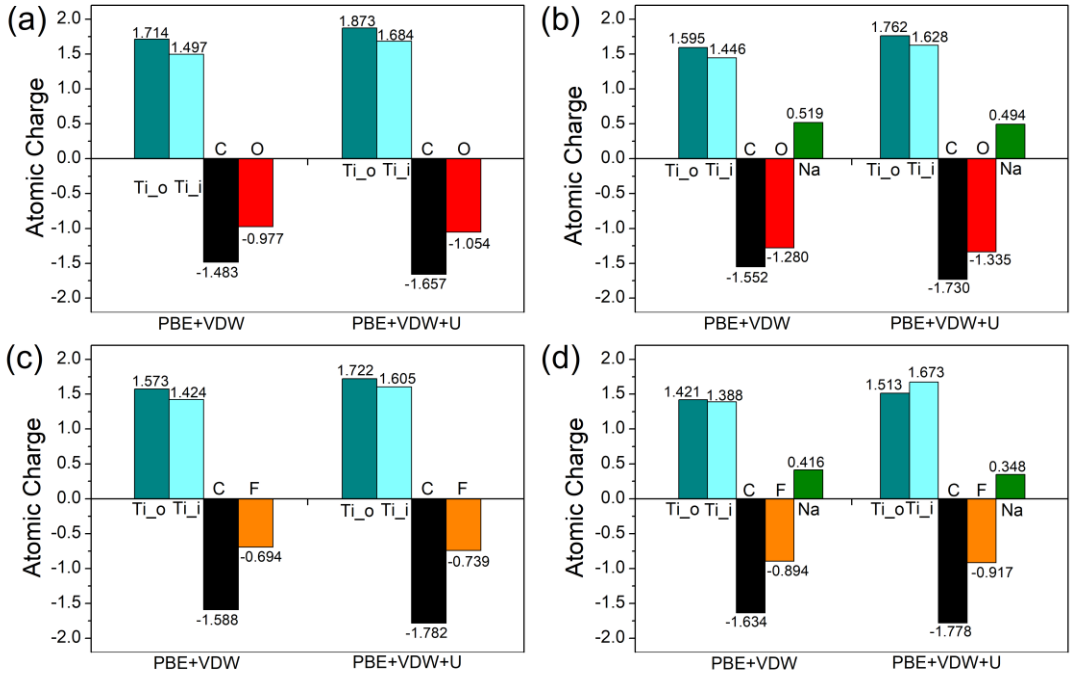

Fig. S16. Atomic charges from both PBE+VDW and PBE+VDW+U in: (a)$Ti_3C_2O_2$; (b) $Ti_3C_2O_2Na_2$; (c)$Ti_3C_2F_2$ and (d)$Ti_3C_2F_2Na_2$. Ti_o refers to titanium atoms in the top and bottom titanium layers, and Ti_i is titanium in the middle layer of titanium in $Ti_3C_2T_2$ (T=O, F). The atomic charge of Ti_o, Ti_i, C, O, F and Na are denoted by dark-cyan, light-cyan, black, red, orange and olive bars respectively.

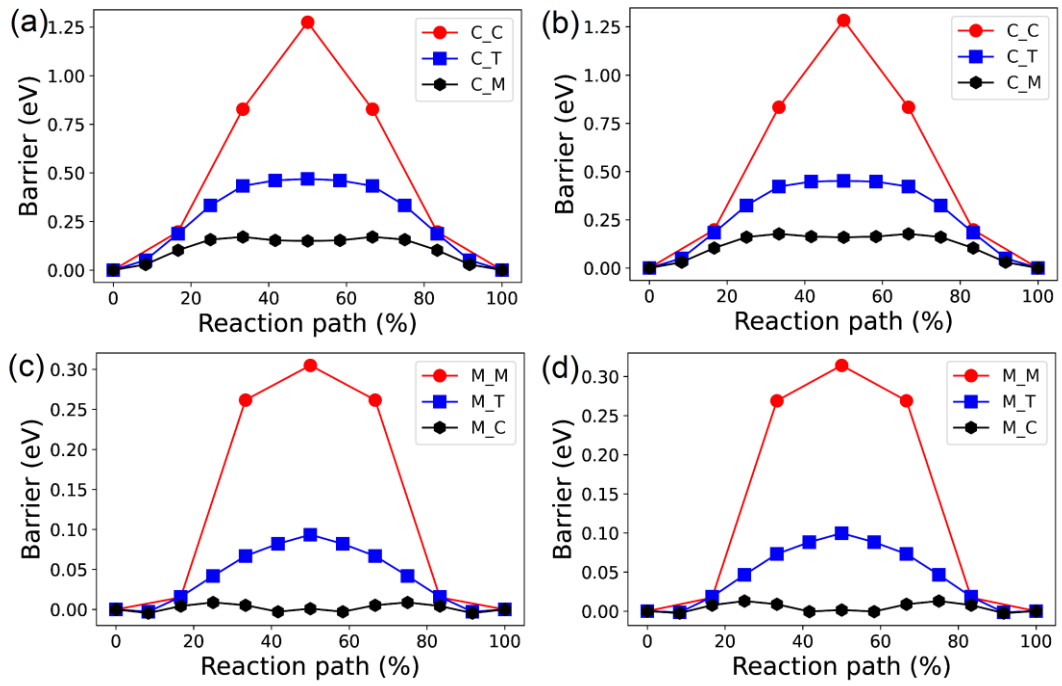

Fig. S17. Migration barriers for: (a) sodium on $Zr_3C_2O_2$ based on PBE+VDW, with

C_C, C_T and C_M migration paths respectively denoted as red circles, blue squares and black hexagons; (b) sodium on $Zr_3C_2O_2$ based on PBE+VDW+U; (c) sodium on $Zr_3C_2(OH)_2$ based on PBE+VDW, with M_M, M_T and M_C migration paths respectively denoted as red circles, blue squares and black hexagons; (d) sodium on $Zr_3C_2(OH)_2$ based on PBE+VDW+U.

For $Zr_3C_2(OH)_2$, the stable location for sodium is on the M-site discussed in the main text, and thus the corresponding migration paths are denoted as M_M, M_T and M_C. Similar to previous definition, M_M means that sodium from the M-site migrates to neighbouring M-site directly; M_T denotes that sodium from the stable M-site moves to a neighbouring T-site, and then migrates to another neighbouring M-site. M_C implies that sodium migrates from an M-site to neighbouring C-site, and then moves to another neighbouring M-site.

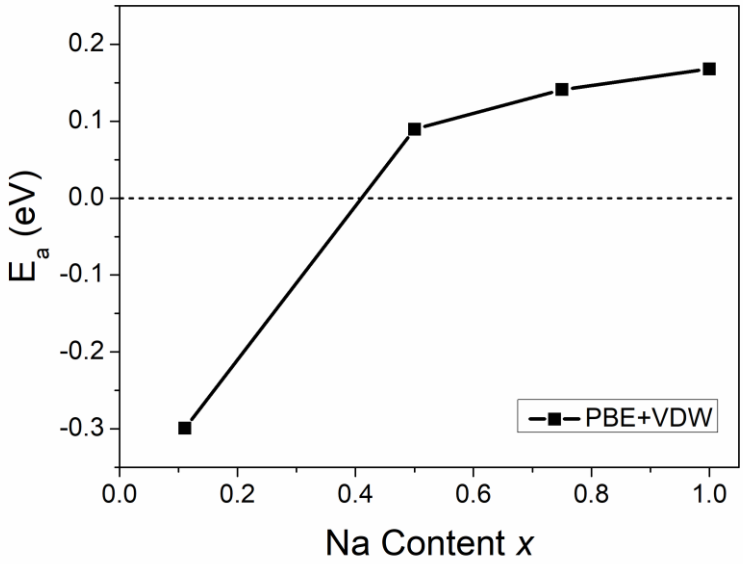

Fig. S18. Adsorption energy of sodium on $Zr_3C_2(OH)_2$ based on PBE+VDW.

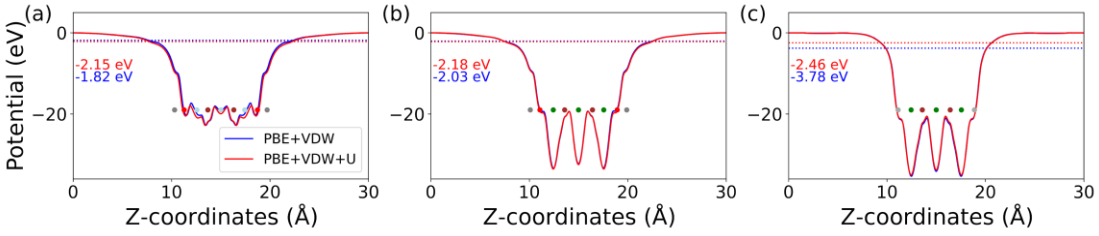

Fig. S19. (a)Average potential along the *c*-axis in $Ti_3C_2(OH)_2$, where the blue and red solid lines show the potential values from PBE+VDW and PBE+VDW+U respectively, while dashed lines represent corresponding Fermi levels relative to vacuum level; (b) and (c) average potentials along the *c*-axis in $Zr_3C_2(OH)_2$ and $Zr_3C_2F_2$ respectively.

Table S4. Atomic charges in $Zr_3C_2F_2$ based on PBE+VDW+U.

Element	Zr_o	Zr_i	C	F
Atomic Charge	2.030	1.840	-2.130	-0.817

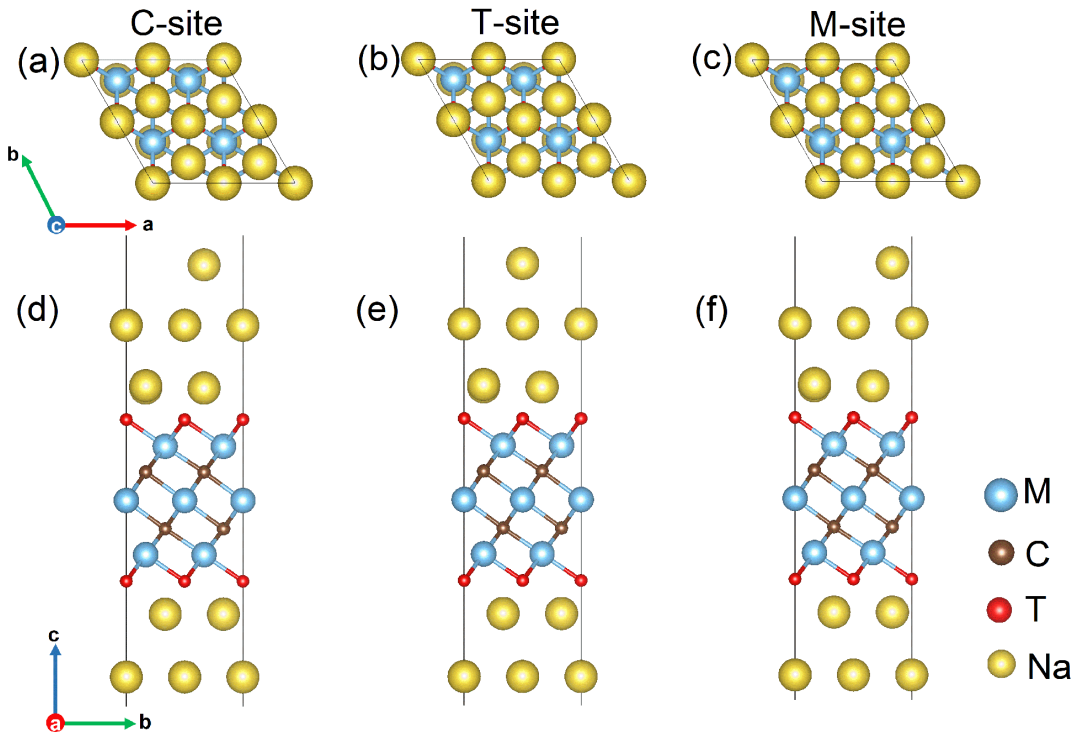

Fig. S20. Possible locations for the third layer of adsorbed sodium: (a) the sodium atom is on the top-site of neighbouring carbon atom, the structure of which is also denoted as C-site. (b) the sodium atom is on the top-site of neighbouring T site, and the structure is denoted as T-site. (c) the sodium atom is on the top-site of neighbouring M atom, and the configuration is denoted as M-site; (d)-(f)corresponding side-views for the structures above.

Table S5. Adsorption energies (in eV) for one sodium atom in the third layer on the 2×2×1 supercells of $Zr_3C_2O_2$ and $Zr_3C_2S_2$ MXenes based on PBE+VDW+U.

Configurations	C-site	T-site	M-site
$Zr_3C_2O_2$	-0.0308	**-0.0362**	-0.0314
$Zr_3C_2S_2$	0.128	**0.0947**	0.129

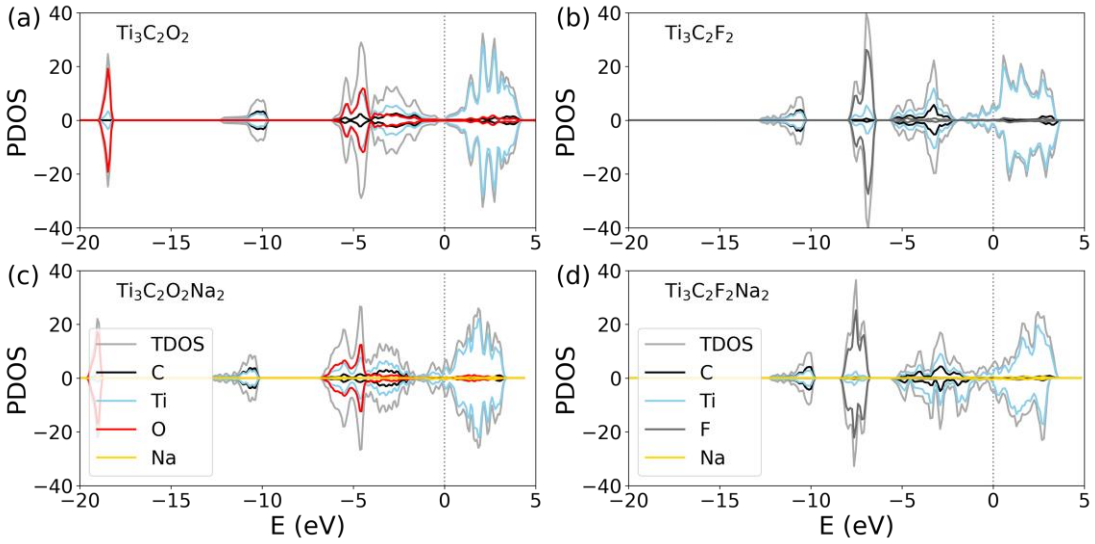

Fig. S21. Densities of states (DOSs) of (a) $Ti_3C_2O_2$, (b)$Ti_3C_2F_2$, (c)$Ti_3C_2O_2Na_2$ and (d)$Ti_3C_2F_2Na_2$ from PBE+VDW+U. The projected DOS from C, Ti, O, F and Na atoms are denoted in black, light blue, red, dark grey and gold lines, respectively.

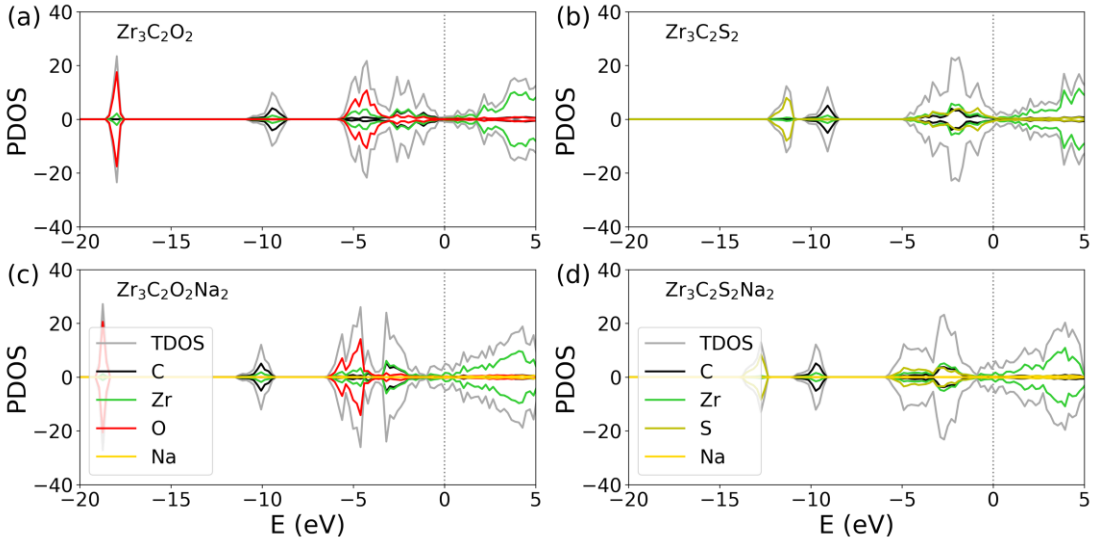

Fig. S22. Densities of states (DOSs) of (a) $Zr_3C_2O_2$, (b) $Zr_3C_2S_2$, (c) $Zr_3C_2O_2Na_2$ and (d) $Zr_3C_2S_2Na_2$ from PBE+VDW+U. The projected DOS from C, Zr, O, S and Na atoms are denoted in black, light green, red, yellow and gold lines, respectively.