Supporting Information

First-principles study of Li-ion storage of functionalized Ti_2C monolayer with vacancies

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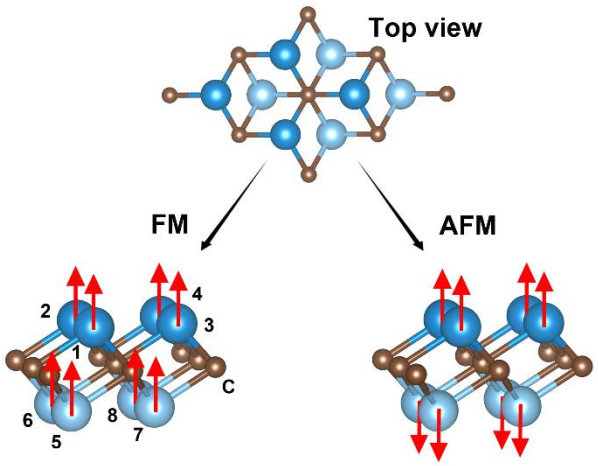

Figure S1. Top and side views of Ti_2C monolayer with ferromagnetic (FM) and antiferromagnetic (AFM) configurations. "↑" and "↓" for the Ti atoms represent two spin directions, corresponding to "+" and "-" in Table S1.

Table S1. Magnetic Configuration [A] and relative energy per formula unit for Ti_2C and Li adsorption energy on the surface of Ti_2C monolayer in ferromagnetic (FM) and antiferromagnetic (AFM1) states.

Type	Ti1	Ti2	Ti3	Ti4	Ti5	Ti6	Ti7	Ti8	ΔE_{tot}(meV/cell)[B]	E_{ad}(eV)[C]
NM	0	0	0	0	0	0	0	0	0	
FM	+	+	+	+	+	+	+	+	-110	-2.26
AFM1	+	+	+	+	-	-	-	-	-137	-2.31
AFM2	-	+	+	-	-	+	+	-	-25	
AFM3	-	+	+	-	+	-	-	+	-21	
AFM4	-	+	+	-	-	+	-	+	-30	
AFM5	-	+	+	-	+	-	+	-	-25	
AFM6	-	+	-	+	-	+	-	+	5	
AFM7	-	+	-	+	+	-	+	-	6	

[A] Labels "Ti1-Ti8" are marked in Figure 1a. In this table, "+" represents the upward direction of magnetic moment along the *z* direction as been mentioned above. Conversely, "-" means the downward direction.

[B] ΔE_{tot} indicates the difference of total energy per formula unit for Ti_2C compared with nonmagnetic.

[C] Adsorption energy of Li atom on the surface of Ti_2C monolayer in different magnetic states. A 2×2 Ti_2C cell is used to calculate.

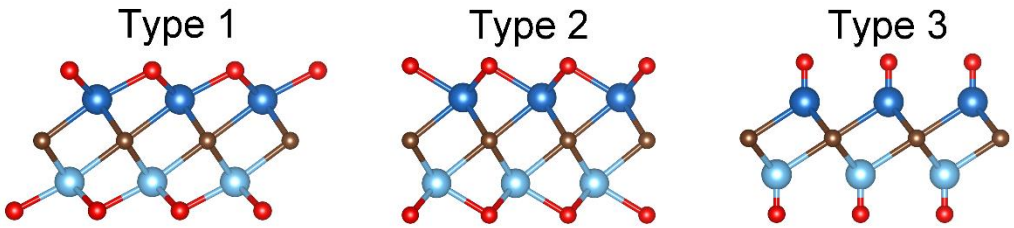

Figure S2. Three considered types of Ti_2CT_2 (T = O, F and OH).

Table S2. The difference of total energy per formula unit for Ti_2CT_2 of the considered types of Ti_2CT_2 monolayers. Due to the Type 3 is unstable by the geometry optimization, we just compare the energy between Type 1 and Type 2. A 3×3 Ti_2C cell is used to calculate.

	O	F	OH
Type 1 (eV/cell)	-1.745	-0.531	-0.290
Type 2 (eV/cell)	0	0	0

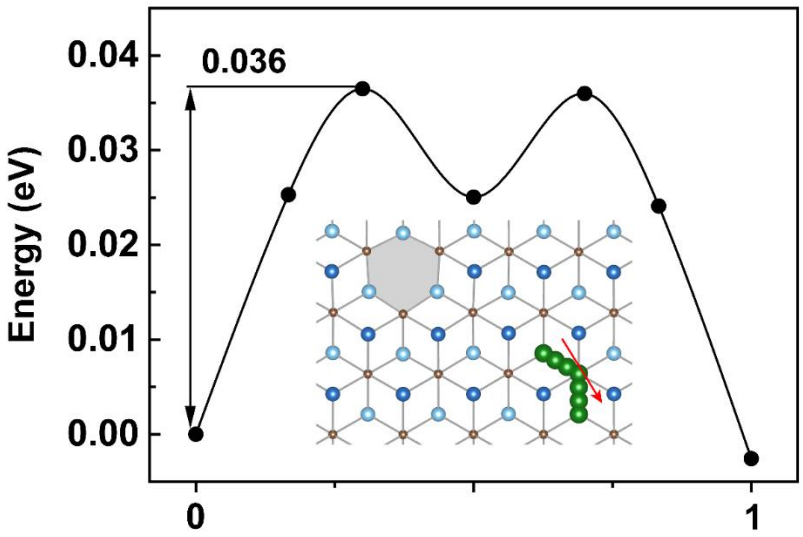

Figure S3. Diffusion barriers of Li on Ti_2C monolayers when Li bypasses titanium vacancy V_{Ti}.

Table S3. Energy barriers for Li diffusion on the Ti_2C and Ti_2CT_2 (T= F or OH) monolayers with different vacancies (V_C and V_{Ti}).

	V_C		V_{Ti}	
	Path	Energy Barrier (eV)	Path	Energy Barrier (eV)
Ti_2C	a→b	0.085	a→b	0.473
	b→c	0.068	b→c	0.104
	c→b	0.163	c→b	0.086
	b→a	0.093	b→a	0.016
Ti_2CF_2	a→b	0.218	a→b	0.162
	b→c	0.061	b→c	0.204
	c→d	0.135	c→d	0.023
	d→e	0.154	d→c	1.192
	e→d	0.180	c→b	0.011
	d→c	0.071	b→a	0.484
	c→b	0.256		
	b→a	0.046		
$Ti_2C(OH)_2$	a→b	0.025	a→b	0.242
	b→a	0.037	b→c	0.048
			c→d	0.046
			d→e	0.413
			e→d	0.169
			d→c	0.598
			c→b	0.113
			b→a	1.011

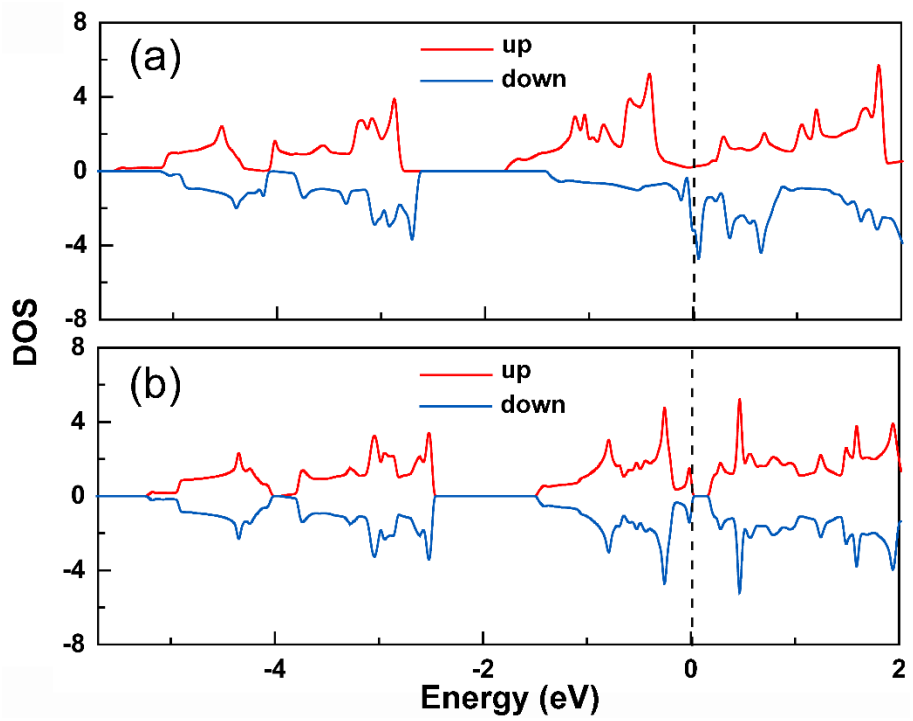

Figure S4. Total density of states (DOS) of Ti_2C monolayer with (a) ferromagnetic (FM) and (b) antiferromagnetic (AFM) configurations.

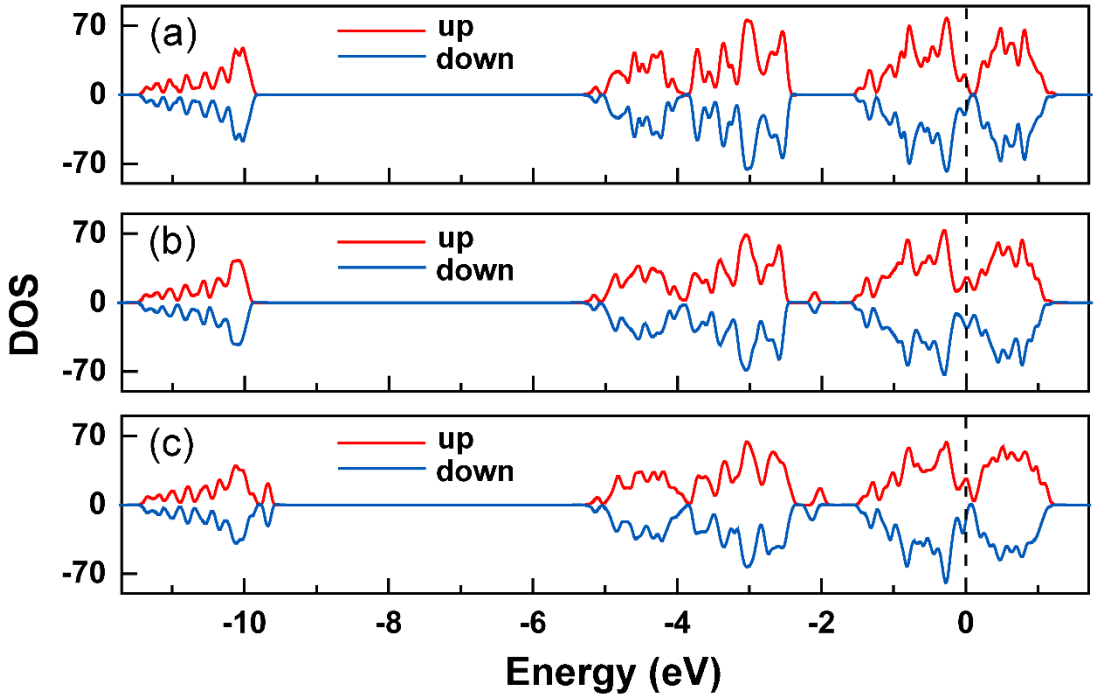

Figure S5. Total density of states of (a) pristine Ti_2C monolayer, (b) with carbon vacancy and (c) with titanium vacancy.

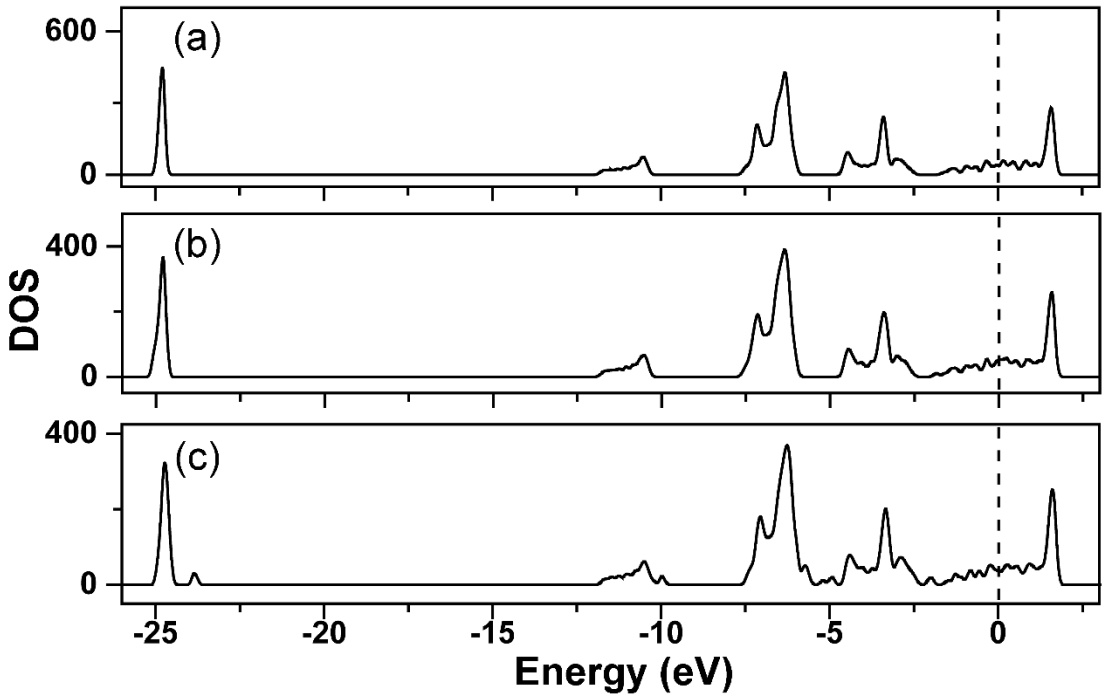

Figure S6. Total density of states of (a) pristine Ti_2CF_2 monolayer, (b) with carbon vacancy and (c) with titanium vacancy.

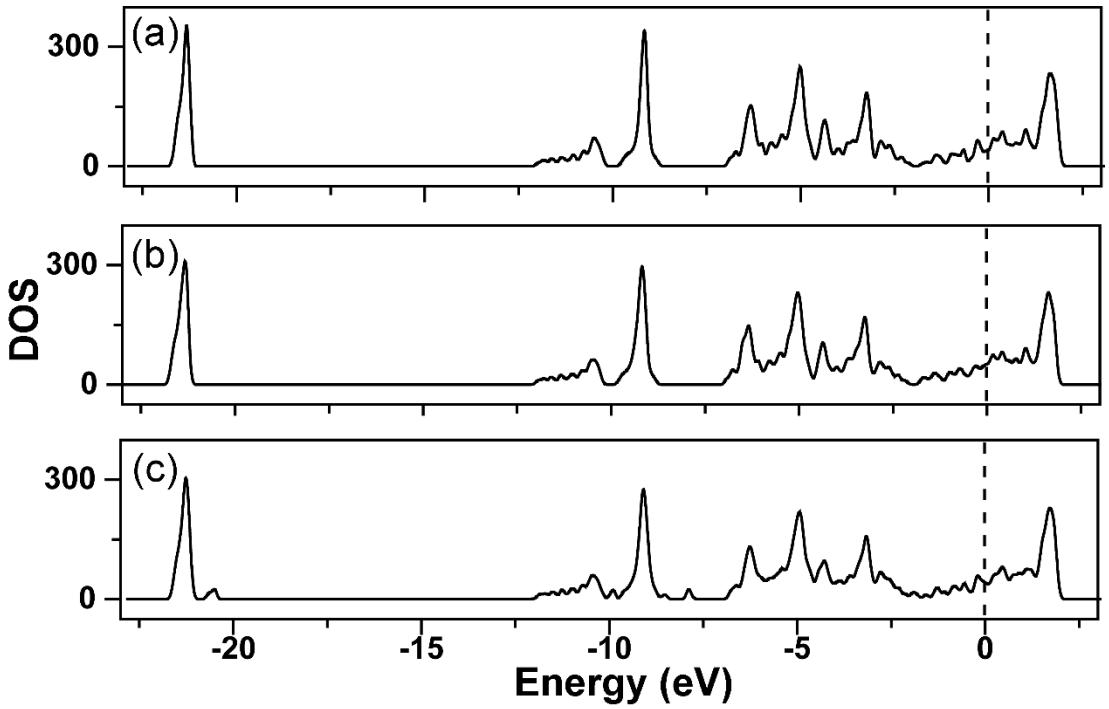

Figure S7. Total density of states of (a) pristine $Ti_2C(OH)_2$ monolayer, (b) with carbon vacancy and (c) with titanium vacancy.

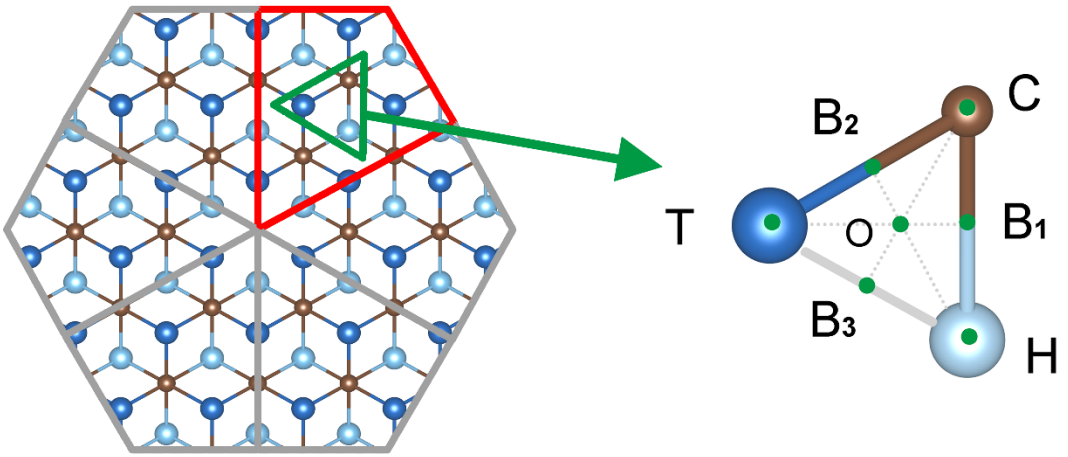

Figure S8. The details of depicting the color filled contour plots of adsorption energy.

Taken the situation of Li on Ti_2C monolayers with carbon vacancy as an example, we describe the details of depicting the color filled contour plots of adsorption energy. According to the symmetry, we only choose the area outlined with red quadrilateral to calculate the adsorption energy of Li at specific sites, including sites on top of the atoms (T, H and C sites), on top of the middle point of two neighboring atoms (B1, B2 and B3 sites), and on top of the center of three neighboring atoms (O site). The schematic illustration is shown in Figure S8. Based on the adsorption energy of Li at these sites, a cubic interpolation is applied to depict the color filled contour plots using Matlab (Version R2012a). The final contour plot in the hexagonal area is constructed by the contour plot within the area of red quadrilateral under the symmetry operation. The plots for Li adsorption on other surfaces as concerned in this work are depicted using the same method.