Supporting Information

Origin of theoretical pseudocapacitance of two-dimensional supercapacitor electrode $Ti_3C_2T_2$ (T=bare, O, S)

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1. Core level method to calculate the work function of the charged electrode

The WF of charged $Ti_3C_2O_2$ is calculated by the following equations:

$$\Delta E = \frac{\frac{\Delta E_{Ti(1)\_1s} + \Delta E_{Ti(2)\_1s}}{2} + \Delta E_{C\_1s} + \Delta E_{O\_1s}}{3} \qquad (1)$$

where $\Delta E_{Ti(1)\_1s}$, $\Delta E_{Ti(2)\_1s}$, ΔE_{C_1s} and ΔE_{O_1s} are the energies of 1s orbital of Ti(1), Ti(2), C and O atoms, respectively.

$$\Delta E_F = E_{F_{Ti_3C_2O_2^{-n}}} - E_{F_{Ti_3C_2O_2}} \qquad (2)$$

where $E_{F_{Ti_3C_2O_2^{-n}}}$ and $E_{F_{Ti_3C_2O_2}}$ are the Fermi level of the charged and neutral $Ti_3C_2O_2$, respectively.

The work function of a charged electrode could be calculated by

$$WF = WF_{Ti_3C_2O_2} - (\Delta E_F - \Delta E) \qquad (3)$$

2. Figures and Tables

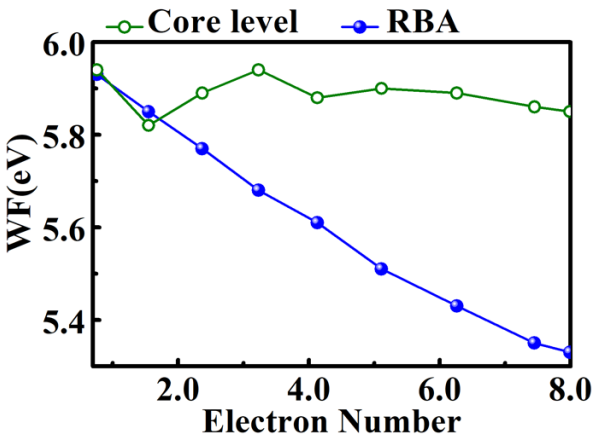

Figure S1 The work function of a charged electrode calculated by core level method (green circles) and rigid band approximation method (blue dots) versus charge value in $Ti_3C_2O_2$.

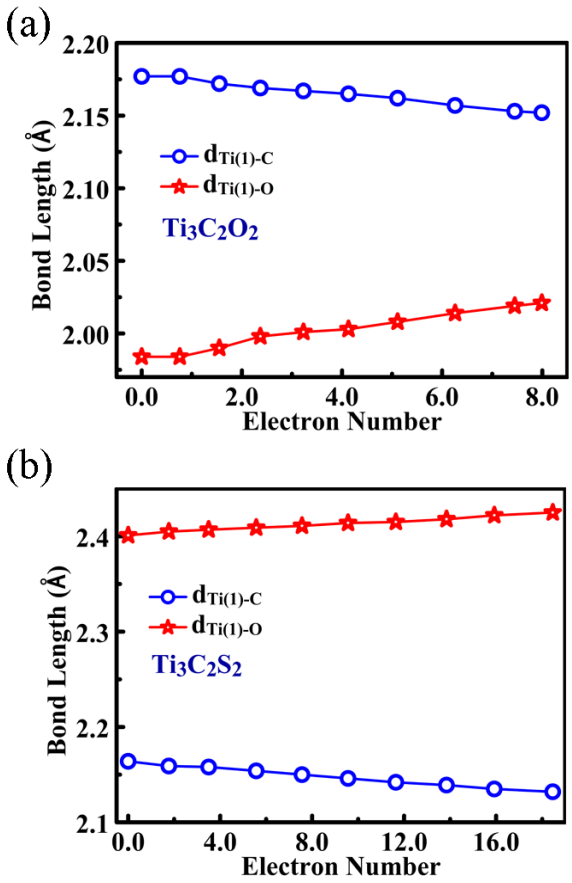

Figure S2 Atomic bond lengths of the charged $Ti_3C_2T_2$ (T=O, S). Blue circles and red stars are the bond lengths of Ti(1)-C and Ti(1)-O, respectively.

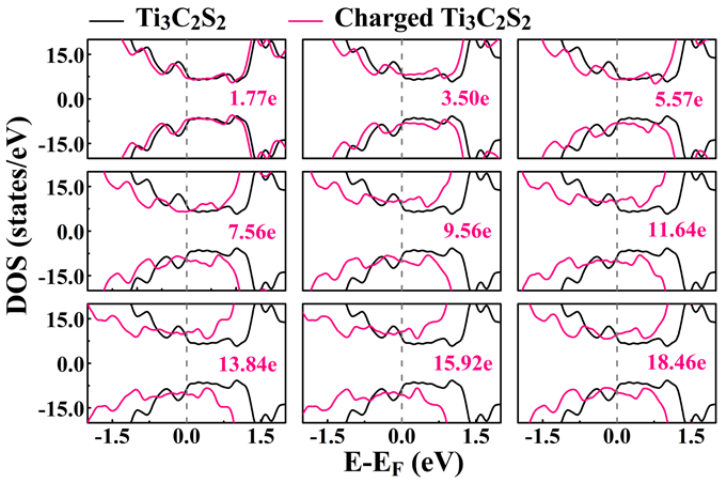

Figure S3 Total density of states (TDOS) of $Ti_3C_2S_2$ before (black lines) and after (pink lines) charging. The number indicates the charge value.

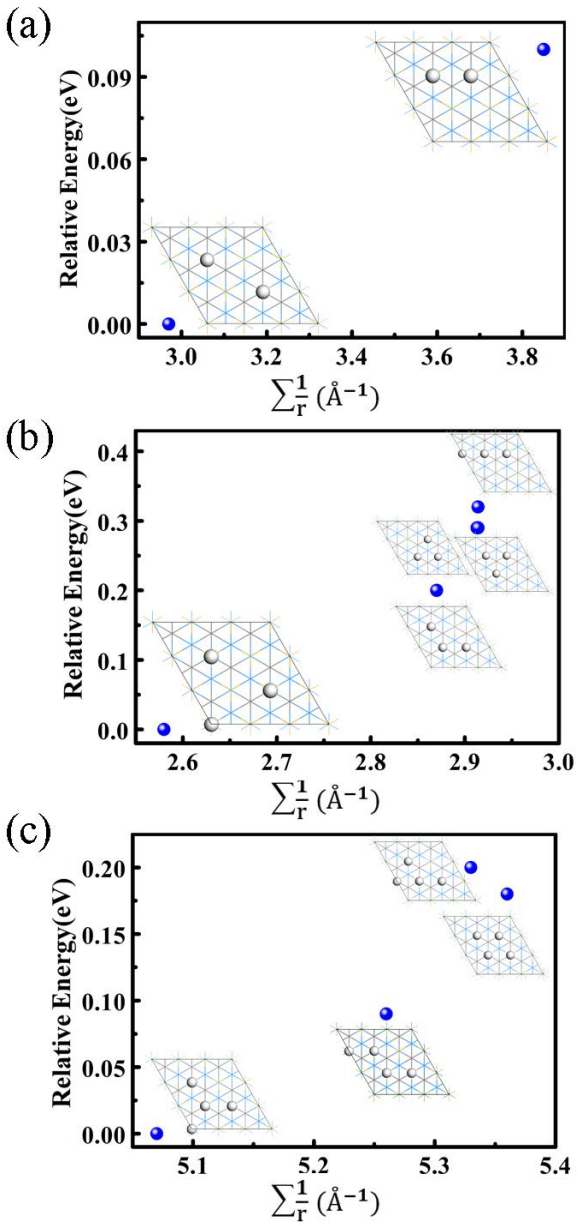

Figure S4 Patterns of $Ti_3C_2S_2$ with (a) two (b) three and (c) four hydrogen ions adsorbed on the top surface. Blue dots are the relative energy of different H patterns. Due to Coulomb repulsion between ions, the energies of different configurations are almost linearly related to the reciprocal distance between hydrogen ions.

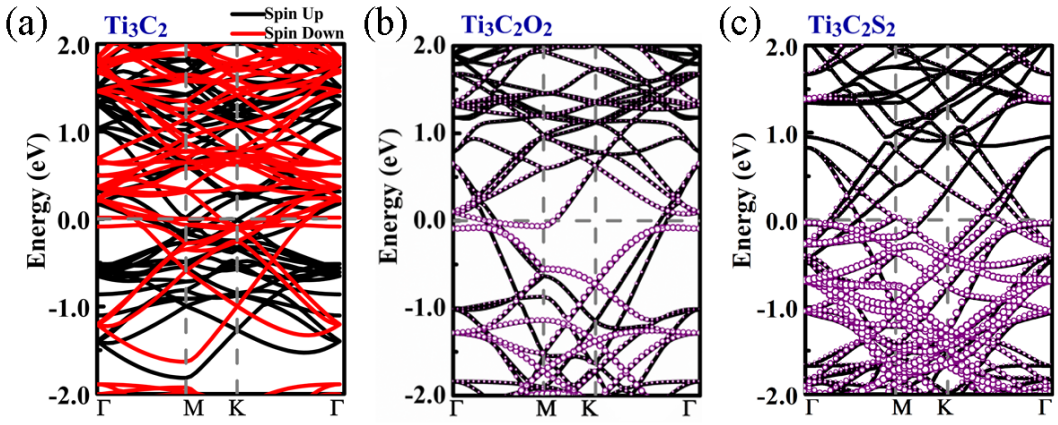

Figure S5 Band structures of $Ti_3C_2T_2$ (T=bare, O, S). The violet circles represent the contributions of oxygen and sulphur atoms, respectively.

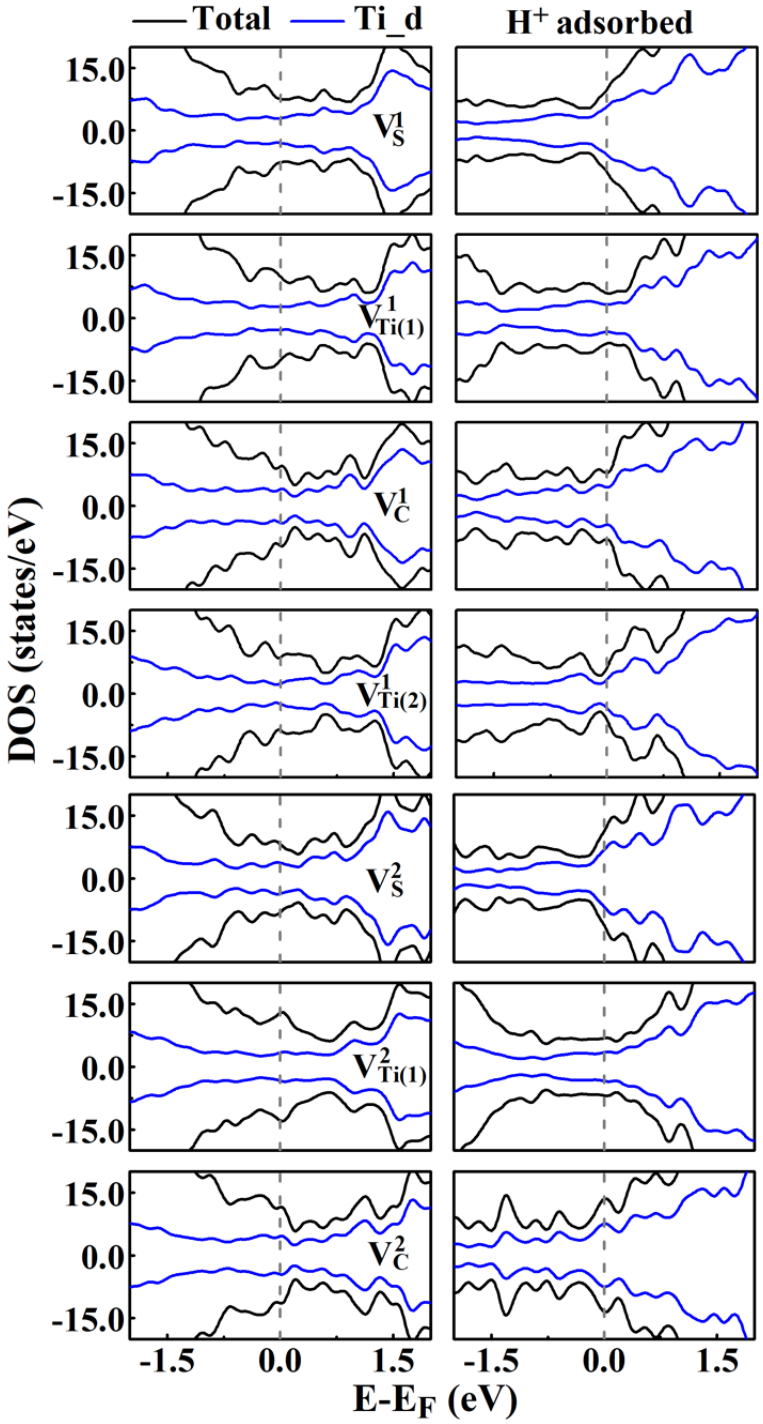

Figure S6 Electronic structures of $Ti_3C_2S_2$ with different atom vacancies before and after hydrogen ions adsorption. V represents the atom vacancy and the number "1" represents one vacancy on the top surface and the number "2" represents one vacancy on both top and bottom surfaces.

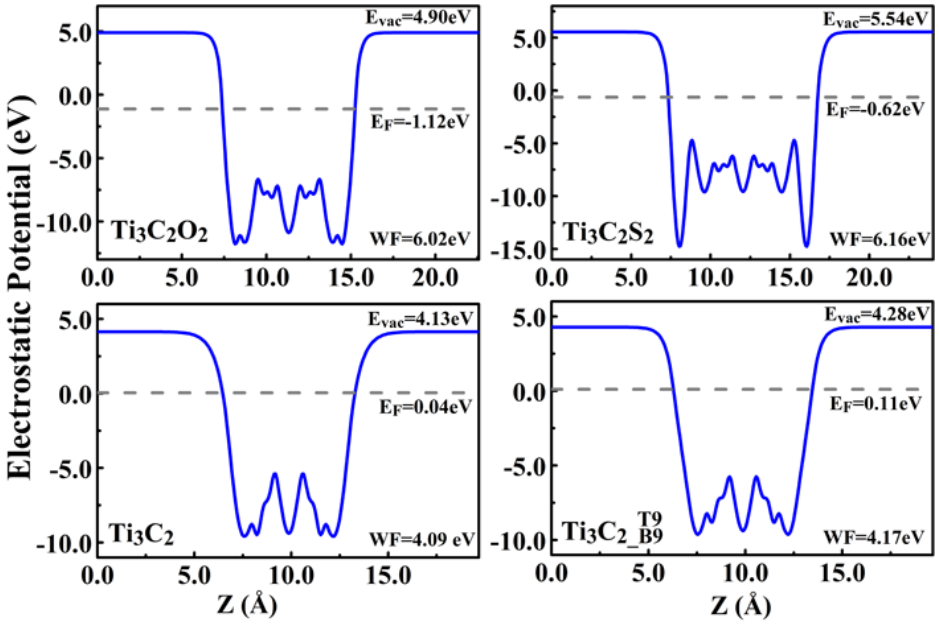

Figure S7 The average electrostatic potential along c axis (blue solid line) and Fermi level (grey broken line) of $Ti_3C_2O_2$, $Ti_3C_2S_2$, Ti_3C_2 and $Ti_3C_{2\_B9}^{T9}$.

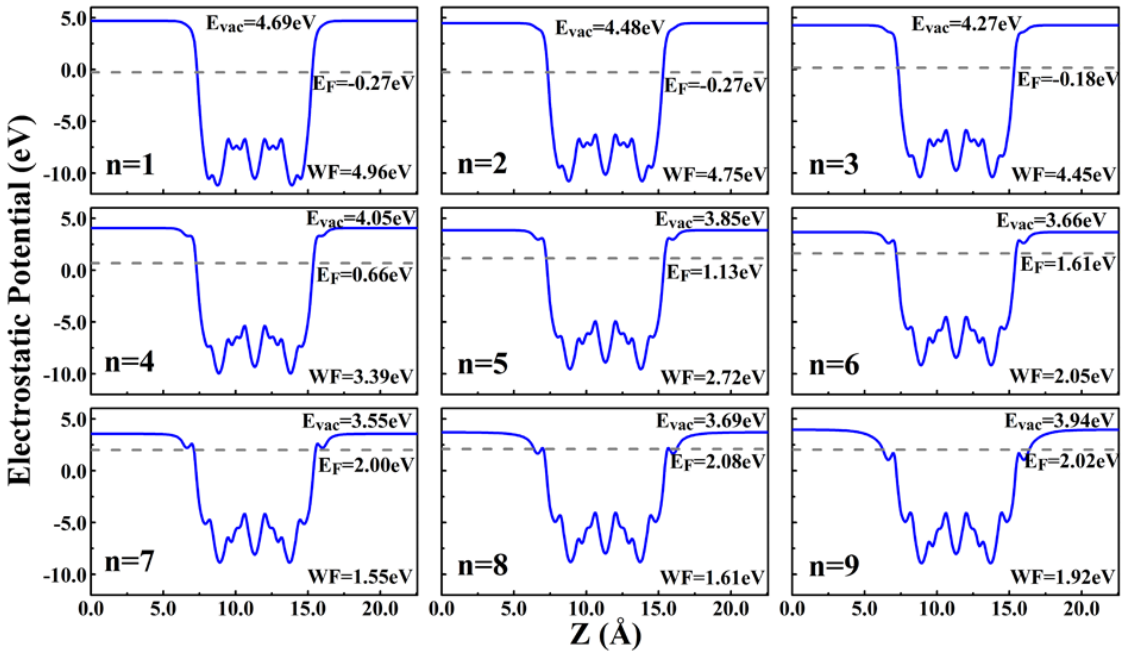

Figure S8 The average electrostatic potential along c axis (blue solid line) and Fermi level (grey broken line) of $Ti_3C_2O_{2\_Bn}^{Tn}$ (n=1~9).

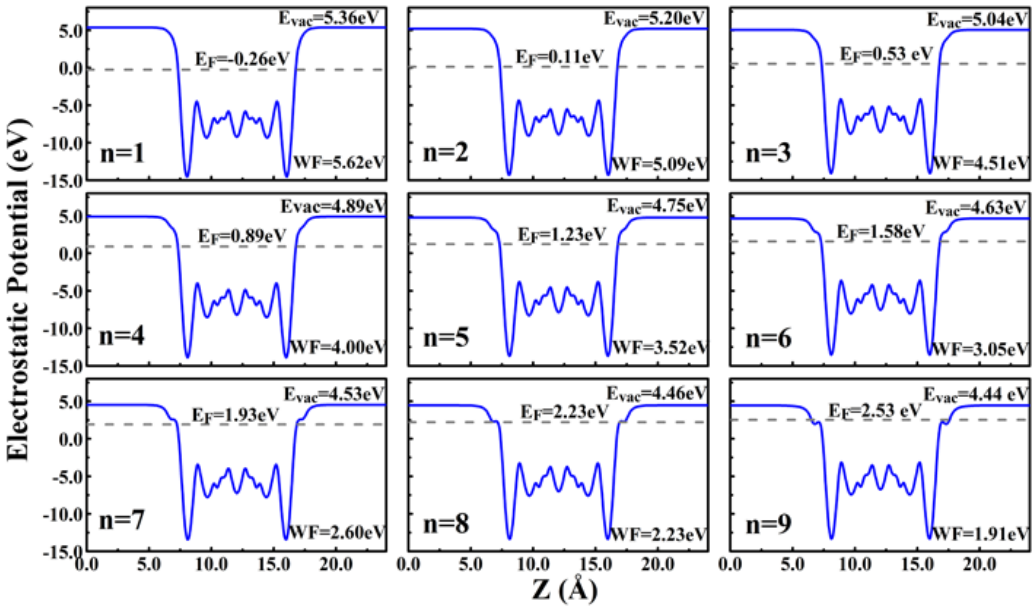

Figure S9 The average electrostatic potential along c axis (blue solid line) and Fermi level (grey broken line) of $Ti_3C_2S_{2\_Bn}^{Tn}$ (n=1~9).

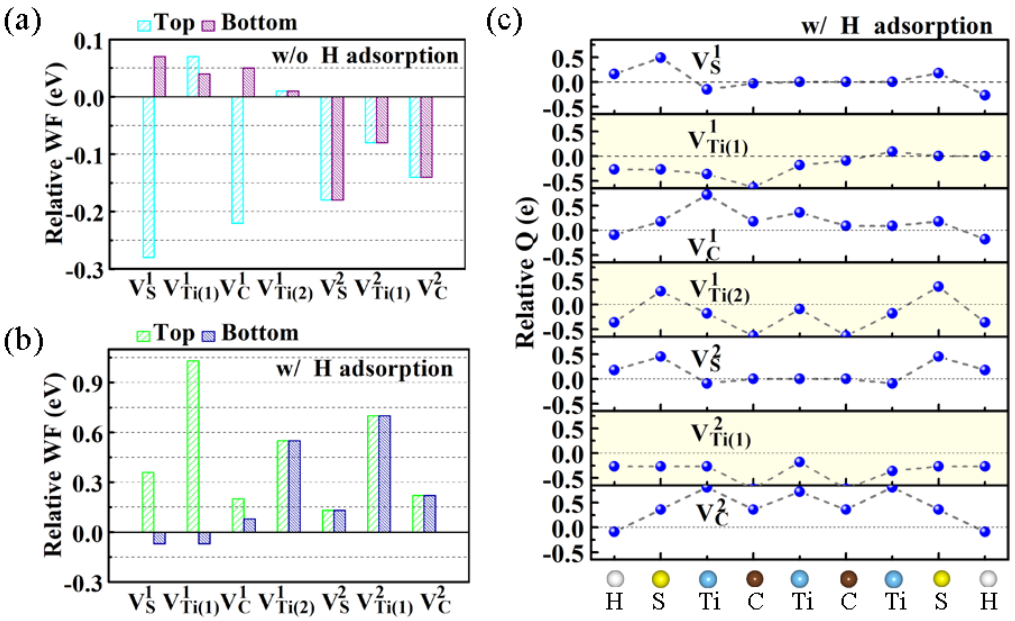

Figure S10 The work function of top and bottom surface in defective $Ti_3C_2S_2$ relative to that in pristine one (a) before and (b) after H adsorption. (c) Variation of numbers of electrons in different atom layers of defective $Ti_3C_2S_2$ with H adsorption relative to those of pristine one.

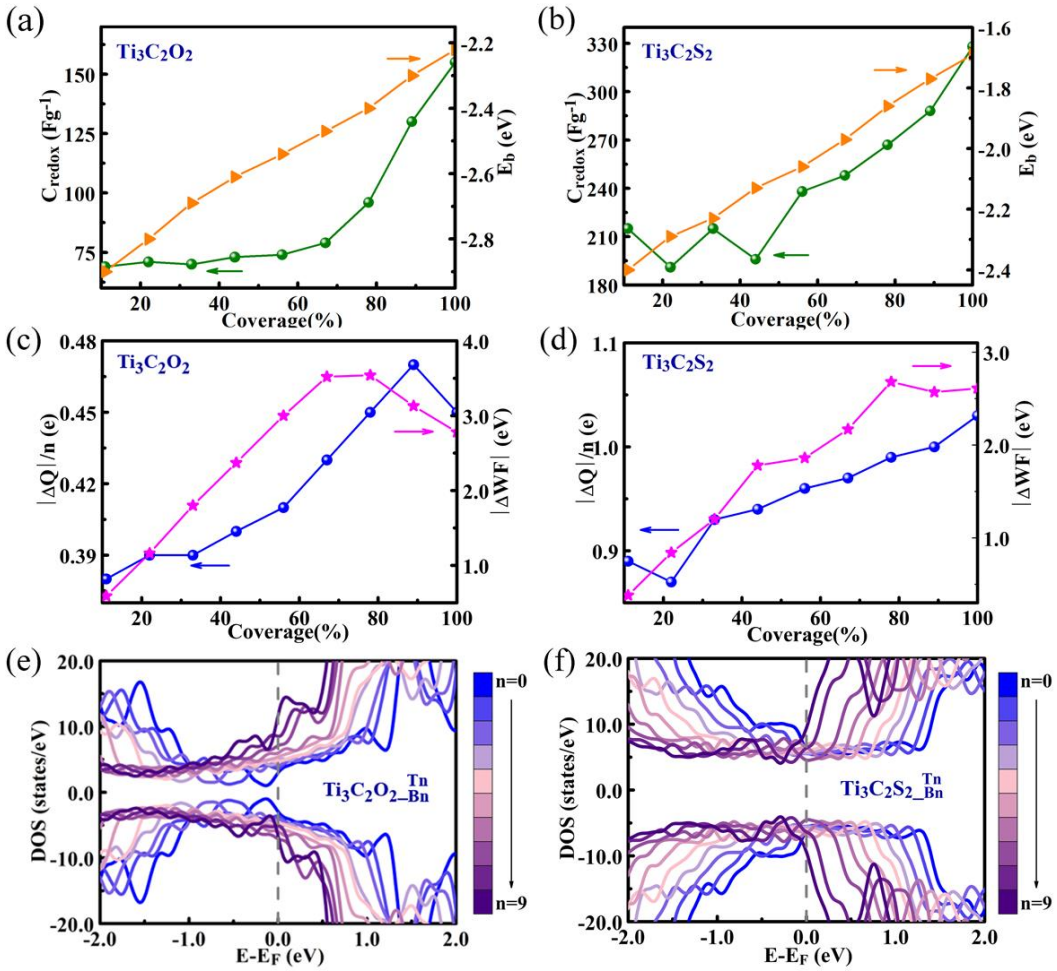

Figure S11 The calculated results of $Ti_3C_2O_2$ and $Ti_3C_2S_2$ with the schemes of DFT+U (U=4eV): Pseudocapacitances and binding energies of (a) $Ti_3C_2O_2$ and (b) $Ti_3C_2S_2$. Average transferred charge and variations of work function of (c) $Ti_3C_2O_2$ and (d) $Ti_3C_2S_2$. Total density of states (TDOS) of (e) $Ti_3C_2O_2$ and (f) $Ti_3C_2S_2$ before and after hydrogen ions adsorbed.

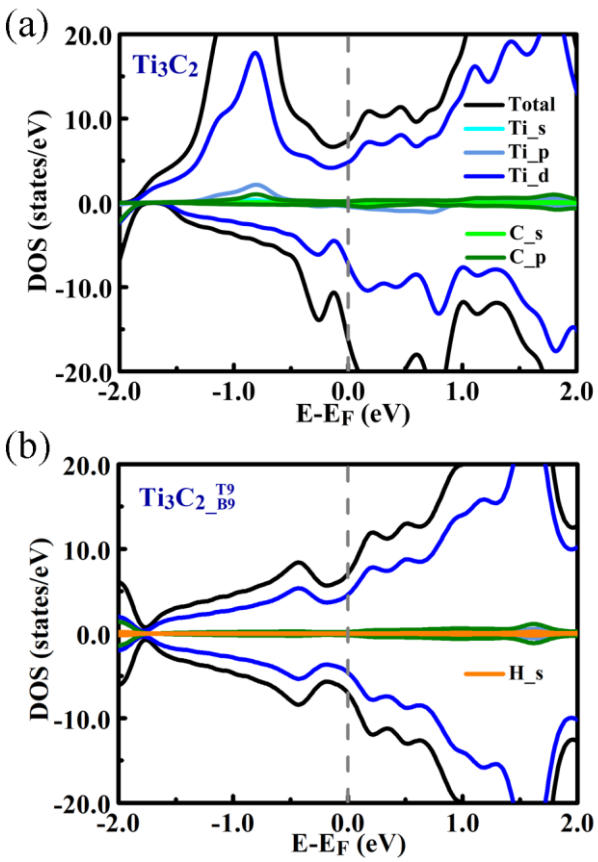

Figure S12 Density of states of Ti_3C_2 (a) before and (b) after hydrogen ions adsorbed calculated with the schemes of GGA+U (U=4eV).

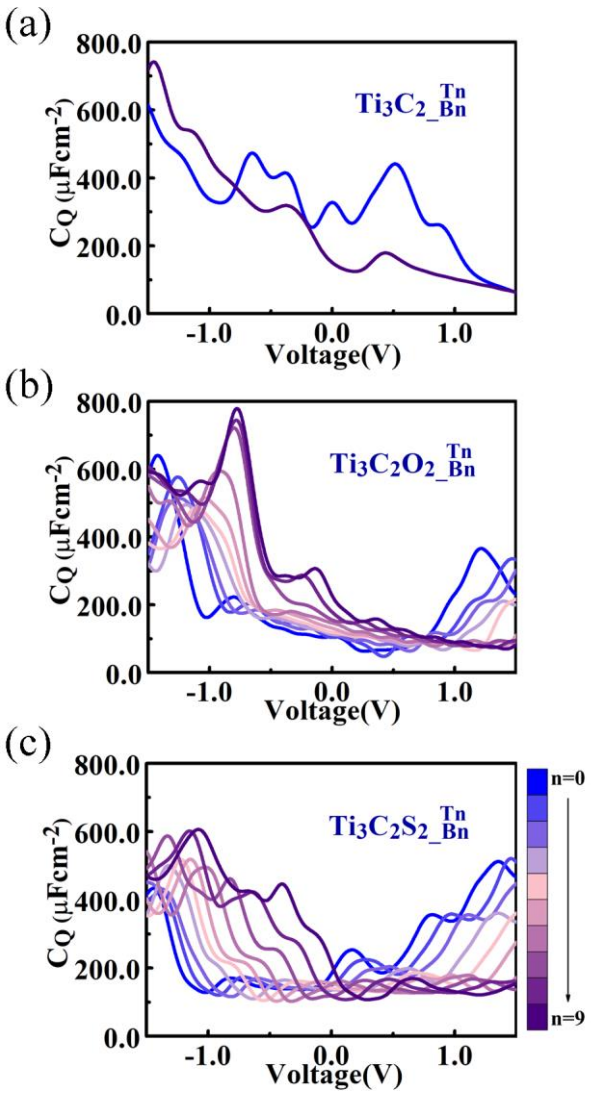

Figure S13 Quantum capacitance of $Ti_3C_2T_2$ (T=bare, O, S) absorbed with hydrogen ions.

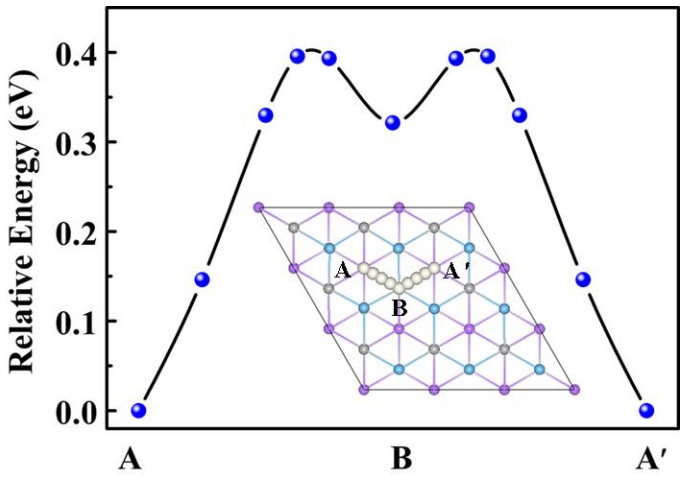

Figure S14 Hydrogen migration path and corresponding energy barrier on the surface of pure Ti_3C_2. Blue, violet, grey and white atoms represent Ti(1), Ti(2), C and H, respectively.

Table S1 The energy of the core level of each element of neutral and charged $Ti_3C_2O_2$.

ΔQ	Ti(1) (eV)			Ti(2) (eV)			C (eV)	O (eV)	ΔE	ΔE_F	WF
(e)	1s	2s	2p	1s	2s	2p	1s	1s	(eV)	(eV)	(eV)
-	−4865.68	−533.78	−441.08	−4864.77	−532.78	−440.10	−265.80	−507.26	-	-	-
0.76	−4864.68	−532.75	−440.09	−4863.75	−531.76	−439.07	−264.80	−506.30	0.99	0.08	5.94
1.55	−4863.72	−531.81	−439.12	−4862.77	−530.78	−438.09	−263.84	−505.35	1.89	0.20	5.82
2.37	−4863.39	−531.48	−438.78	−4862.46	−530.47	−437.78	−263.53	−505.00	2.28	0.13	5.89
3.23	−4863.42	−531.51	−438.81	−4862.50	−530.50	−437.81	−263.59	−505.05	2.23	0.08	5.94
4.13	−4863.40	−531.49	−438.80	−4862.48	−530.48	−437.79	−263.58	−505.04	2.24	0.14	5.88
5.11	−4863.32	−531.41	−438.71	−4862.40	−530.40	−437.71	−263.52	−504.96	2.32	0.12	5.90
6.26	−4863.28	−531.37	−438.67	−4862.37	−530.37	−437.68	−263.51	−504.92	2.34	0.13	5.89
7.45	−4863.25	−531.33	−438.63	−4862.34	−530.34	−437.65	−263.50	−504.90	2.36	0.16	5.86
7.99	−4863.24	−531.33	−438.63	−4862.33	−530.33	−437.64	−263.51	−504.90	2.36	0.17	5.85

Table S2 The work function of a charged electrode calculated by the Integrated DOS method with different DOS grid points.

ΔQ (e)	NEDOS=2000			NEDOS=5000		
	Integrated ΔQ (e)	ΔE_F (eV)	WF (eV)	Integrated ΔQ (e)	ΔE_F (eV)	WF (eV)
0.76	0.63	0.07	5.95	0.75	0.09	5.93
1.55	1.61	0.18	5.84	1.51	0.17	5.85
2.37	2.33	0.25	5.77	2.33	0.25	5.77
3.23	3.05	0.31	5.71	3.29	0.34	5.68
4.13	4.22	0.42	5.60	4.06	0.41	5.61
5.11	5.07	0.49	5.53	5.17	0.51	5.51
6.26	6.49	0.59	5.43	6.24	0.59	5.43
7.45	7.60	0.66	5.36	7.45	0.67	5.35
7.99	8.20	0.69	5.33	7.88	0.69	5.33

Table S3 The total energy difference of $Ti_3C_2T_2$ (T= O, S) with different surface group sites and formation energy (E_f) of T (T= O, S) in eV, of unit cell.

	T site		E_f
	Top_Ti	Top_C	
$Ti_3C_2O_2$	0	1.47	-9.82
$Ti_3C_2S_2$	0	0.94	-4.78

Table S4 The binding energy of one hydrogen ion adsorbed on $Ti_3C_2T_2$ (T=bare, O, S) monolayer. The top of T (T=O, S) atom is the same site as the top of the Ti(2) atom.

adsorption sites	$Ti_3C_2O_2$	$Ti_3C_2S_2$	Ti_3C_2
Top_T	-2.93	-2.48	-
Bridge	-2.17	-2.31	-2.68
Hollow	-0.53	-2.41	-3.25
Top_Ti(1)	-0.07	-2.42	-2.23
Top_Ti(2)	-	-	-3.57

Table S5 The binding energy of $Ti_3C_2T_2$ (T=O, S) with H adsorption on the top and bottom surfaces. n is the number of H adsorbed on each surface. T and B refer to the top and bottom surface, respectively.

n	$Ti_3C_2O_{2\_}^{Tn}{}_{Bn}$	$Ti_3C_2S_{2\_}^{Tn}{}_{Bn}$
2	-2.90	-2.40
4	-2.79	-2.29
6	-2.76	-2.23
8	-2.66	-2.13
10	-2.59	-2.06
12	-2.52	-1.97
14	-2.40	-1.86
16	-2.30	-1.77
18	-2.22	-1.69