Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Computational Screening of Functionalized MXenes to Catalyze the Solid and Non-Solid Conversion Reactions in Cathodes of Lithium-Sulfur Batteries

Lirong Zhang, Wenhui Zhang, Xinzhi Ma, Xitian Zhang*, Jing Wen*

Key Laboratory for Photonic and Electronic Bandgap Materials, Ministry of Education, School of Physics and Electronic Engineering, Harbin Normal University, Harbin 150025, P. R. China

*Email: xtzhangzhang@hotmail.com (X. Zhang); wenj674@hrbnu.edu.cn (J. Wen)

Note 1:

Gibbs free energy can be expressed as:

$$G(T) = H(T) - TS(T) = E_0 + H_{vib}(T) - TS_{vib}(T)$$

where E_0 is electronic energy. H and S represent enthalpy and entropy as a function of temperature T. The subscript *vib* means that the thermodynamic properties of the adsorption models for Li_2S_2/Li_2S with the hosts can be estimated under harmonic approximation, ignoring the contributions of translational and rotational motions to entropy and enthalpy. Vibrational contributions to the entropy (S_{vib}) and enthalpy (H_{vib}) are given by

$$S_{vib}(T) = \sum_i^{3N} \frac{\hbar\omega_i/k_BT}{exp(\hbar\omega_i/k_BT)} - \ln\left[1 - exp\left(\frac{-\hbar\omega_i}{k_BT}\right)\right]$$

$$H_{vib}(T) = \sum_i^{3N} \frac{1}{2}\hbar\omega_i + \hbar\omega_i\left[exp\left(\frac{\hbar\omega_i}{k_BT}\right) - 1\right]^{-1}$$

where $\hbar$ is Plank's constant divided by 2π, k_B represents Boltzmann constant. So, the Gibbs free energy can be transformed to：

$$G(T) = E_0 + ZPE + \Delta H_{0\to T} + TS_{vib}(T)$$

$$ZPE = \sum_i^{3N-3} \frac{1}{2}\hbar\omega_i$$

$$\Delta H_{0\to T} = \sum_i^{3N-3} \hbar\omega_i\left[exp\left(\frac{\hbar\omega_i}{k_BT}\right) - 1\right]^{-1}$$

where *ZPE* represents the zero-point energy, $\Delta H_{0\to T}$ represents the correction of enthalpy at the room temperature of 300 K. The calculated values of E_0, *ZPE*, $\Delta H_{0\to T}$

and S_{vib} in the reaction $1/2(Li_2S_2 + 2Li) \rightarrow Li_2S$ are shown in Table S1, where $E_{Li=}$ -1.91 eV.

Table S1 (a) Calculated values of E_0, *ZPE*, $\Delta H_{0\rightarrow T}$ and S_{vib} based on the adsorption configurations of $Ti_3C_2T_x$-Li_2S_2 (T=H, O, F, S, Cl, Se, Br, and NH).

	$Ti_3C_2H_2$	$Ti_3C_2O_2$	$Ti_3C_2F_2$	$Ti_3C_2S_2$
E_0 (eV)	-509.1422	-605.5889	-557.1856	-544.6192
ZPE (eV)	0.2013	0.1785	0.1719	0.1775
$\Delta H_{0\rightarrow T}$ (eV)	0.1568	0.1527	0.1811	0.1777
S_{vib}(eV/K)	0.0010	0.0011	0.0013	0.0013
	$Ti_3C_2Cl_2$	$Ti_3C_2Se_2$	$Ti_3C_2Br_2$	$Ti_3C_2(NH)_2$
E_0 (eV)	-515.2700	-527.8708	-495.8616	-683.1799
ZPE (eV)	0.1681	0.1766	0.1796	0.2082
$\Delta H_{0\rightarrow T}$ (eV)	0.1582	0.1773	0.1743	0.1592
S_{vib}(eV/K)	0.0011	0.0012	0.0012	0.0011

Table S1 (b) Calculated values of E_0, ZPE, $\Delta H_{0\rightarrow T}$ and S_{vib} based on the adsorption configurations of $Ti_3C_2T_x$-Li_2S (T=H, O, F, S, Cl, Se, Br, and NH).

	$Ti_3C_2H_2$	$Ti_3C_2O_2$	$Ti_3C_2F_2$	$Ti_3C_2S_2$
E_0 (eV)	-504.2282	-600.1382	-552.0974	-540.5736
ZPE (eV)	0.1520	0.1335	0.1295	0.1494
$\Delta H_{0\rightarrow T}$ (eV)	0.1157	0.1300	0.1101	0.1169
S_{vib}(eV/K)	0.0007	0.0009	0.0007	0.0007
	$Ti_3C_2Cl_2$	$Ti_3C_2Se_2$	$Ti_3C_2Br_2$	$Ti_3C_2(NH)_2$
E_0 (eV)	-510.1190	-522.8039	-490.5958	-678.2786
ZPE (eV)	0.1293	0.1378	0.1293	0.1755
$\Delta H_{0\rightarrow T}$ (eV)	0.1357	0.1247	0.1344	0.1089

S_{vib}(eV/K)	0.0010	0.0008	0.0009	0.0007

Table S2 (a) Calculated formation energies of functionalized Ti_3C_2 with 4*e* sites being occupied in unit of eV per formula unit (eV/f.u.).

	$Ti_3C_2H_2$	$Ti_3C_2O_2$	$Ti_3C_2F_2$	$Ti_3C_2S_2$	$Ti_3C_2Cl_2$
$E_{Ti_3C_2T_2}$	-54.83	-65.49	-60.31	-58.77	-55.67
$E_{Ti_3C_2}$	-45.71	-45.71	-45.71	-45.71	-45.71
$2E_T$	-6.77	-8.78	-3.71	-8.08	-3.59
E_f	-2.35	-11.01	-10.88	-4.98	-6.37
	$Ti_3C_2Se_2$	$Ti_3C_2Br_2$	$Ti_3C_2Te_2$	$Ti_3C_2(OH)_2$	$Ti_3C_2(NH)_2$
$E_{Ti_3C_2T_2}$	-57.01	-53.40	-54.69	-72.12	-74.13
$E_{Ti_3C_2}$	-45.71	-45.71	-45.71	-45.71	-45.71
$2E_T$	-6.97	-3.28	-7.28	-15.55	-23.40
E_f	-4.34	-4.41	-1.70	-10.86	-5.02

Table S2 (b) Calculated formation energies of functionalized Ti_3C_2 with 4*f* sites being occupied in unit of eV per formula unit (eV/f.u.).

	$Ti_3C_2H_2$	$Ti_3C_2O_2$	$Ti_3C_2F_2$	$Ti_3C_2S_2$	$Ti_3C_2Cl_2$
$E_{Ti_3C_2T_2}$	-54.00	-63.84	-59.49	-57.95	-55.54
$E_{Ti_3C_2}$	-45.71	-45.71	-45.71	-45.71	-45.71
$2E_T$	-6.77	-8.78	-3.71	-8.08	-3.59
E_f	-1.52	-9.36	-10.07	-4.17	-6.24
	$Ti_3C_2Se_2$	$Ti_3C_2Br_2$	$Ti_3C_2Te_2$	$Ti_3C_2(OH)_2$	$Ti_3C_2(NH)_2$
$E_{Ti_3C_2T_2}$	-56.45	-53.51	-54.71	-67.59	-68.47
$E_{Ti_3C_2}$	-45.71	-45.71	-45.71	-45.71	-45.71
$2E_T$	-6.97	-3.28	-7.28	-15.55	-23.40
E_f	-3.78	-4.52	-1.73	-6.33	0.63

Note 2:

The gas phases were simulated by placing a single molecule (H_2, N_2, O_2, F_2, Cl_2) in a large cubic cell with the lattice constant of 20 Å, where the experimental configurations of H_2, N_2, O_2, F_2, Cl_2 were employed to simulate the initial molecular states of H, N, O, F and Cl. The solid phases were simulated by employing the reported bulk structures, where bulk S was built based on the space group of *Fddd* (No.70), Se based on the space group of $P3_112$ (No.153), and Te based on the space group of $P3_212$ (No.154). According to the experimental density of liquid bromine (3.11 g/cm^3), we randomly placed 4 bromine molecules in a cubic cell with the lattice constant of 7 Å to simulate its liquid phase.

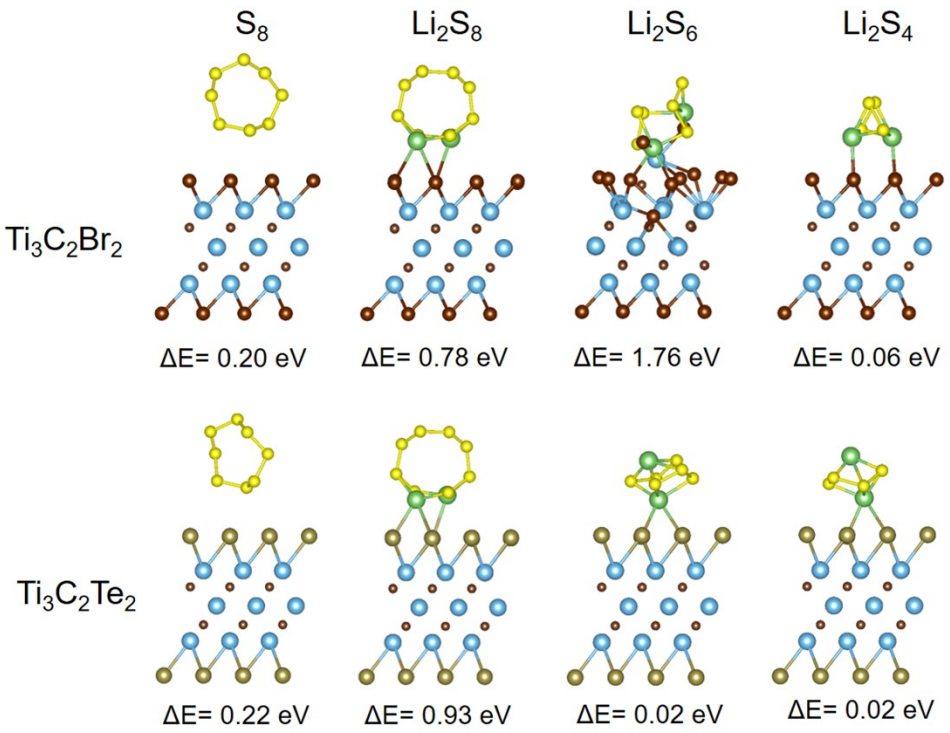

Figure S1 Metastable configurations of $Ti_3C_2Br_2$ and $Ti_3C_2Te_2$ adsorbed by S_8 and Li_2S_x (x=4, 6, and 8), where ΔE represents the energy difference of the metastable adsorption configuration relative to the stable one.

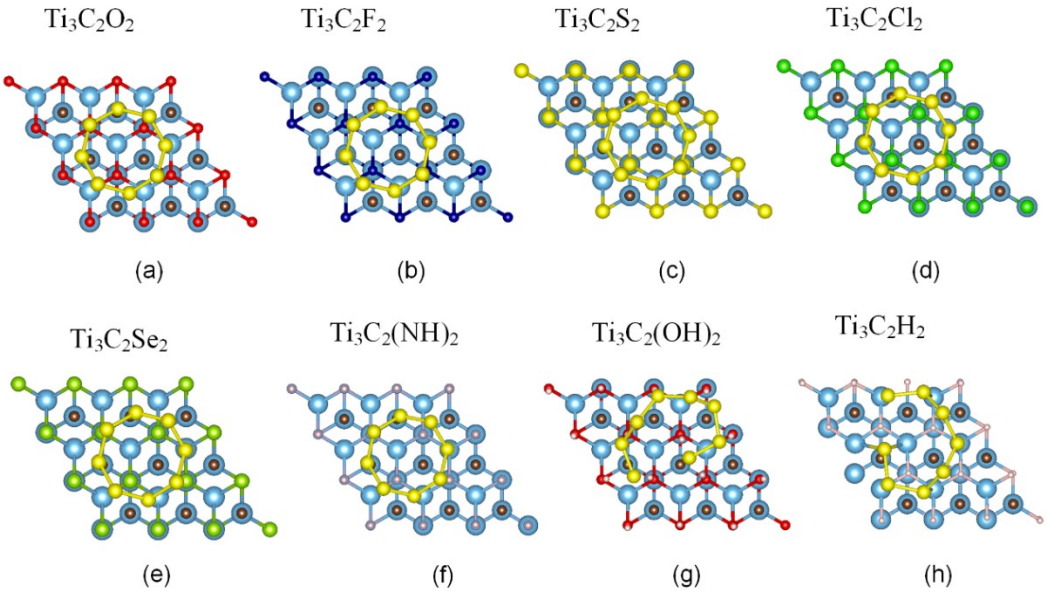

Figure S2. Top views of the adsorption configurations of S_8 on the surfaces of $Ti_3C_2T_2$ (T=O, F, S, Cl, Se, NH, OH, and H).

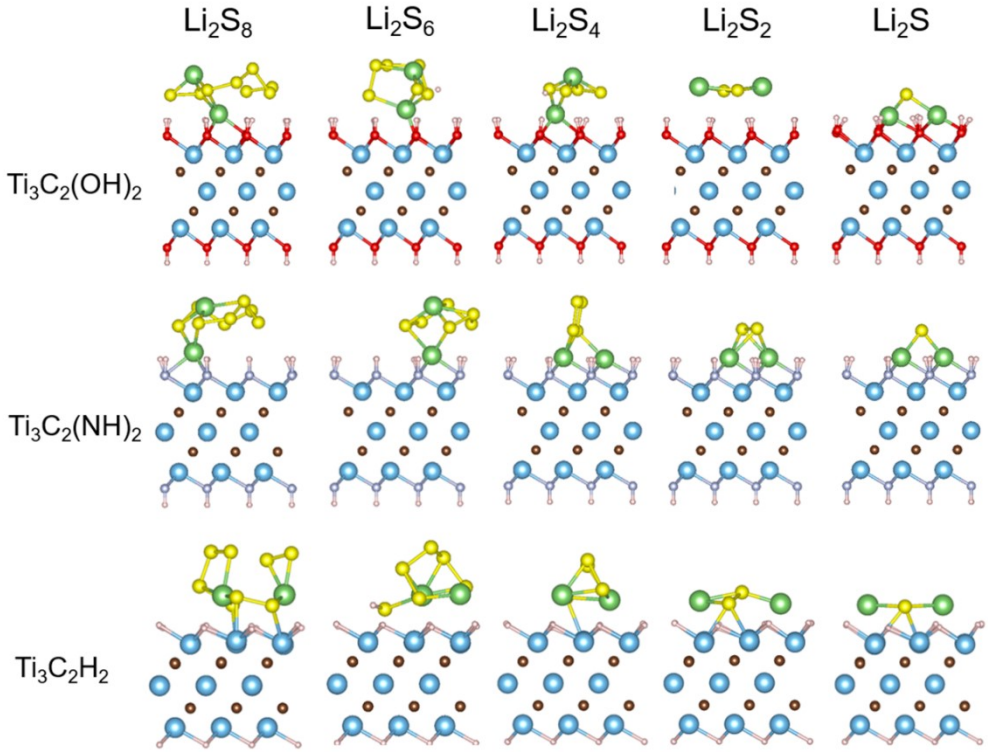

Figure S3 Adsorption configurations of $Ti_3C_2T_2$ (T= OH, NH, and H)-Li_2S_x (x=1, 2, 4, 6, and 8).

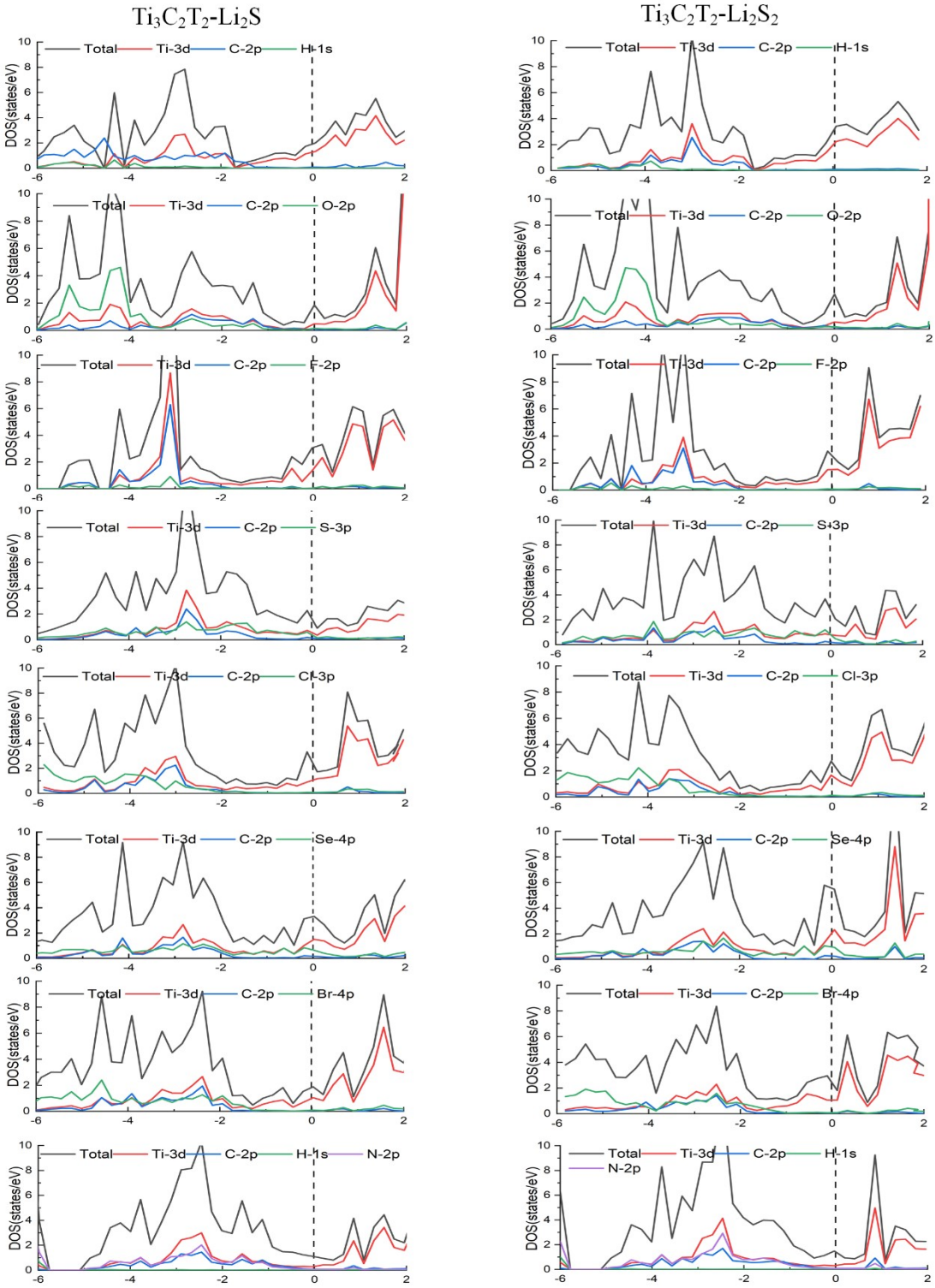

Figure S4 Calculated densities of states (DOS) of the $Ti_3C_2T_2$-Li_2S_2/Li_2S systems (T=H, O, F, S, Cl, Se, Br, NH).

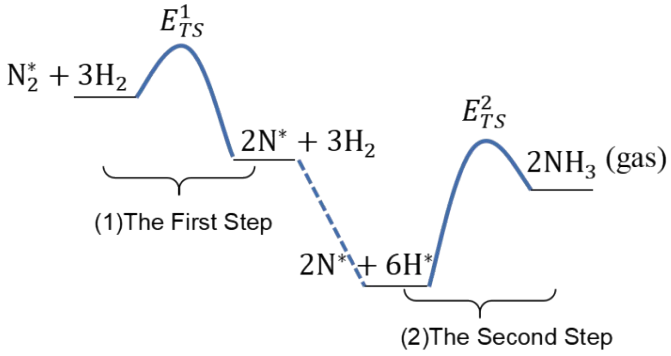

Figure S5 Schematic diagram of the simplified N_2 reduction processes.

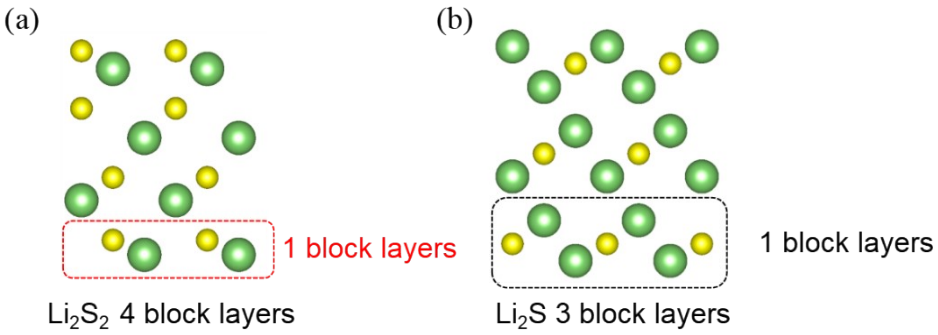

Figure S6 (a) Stabilized Li_2S_2 configuration to simulate its bulk state (4 block layers), (b) Stabilized Li_2S configuration to simulate its bulk state (3 block layers).

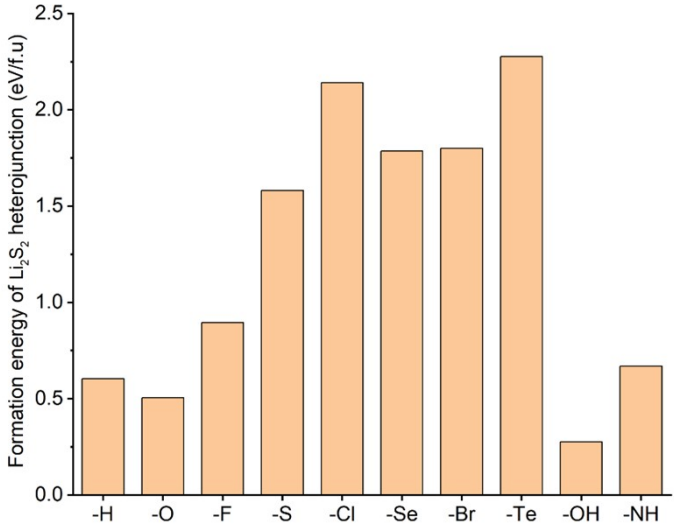

Figure S7 Calculated formation energies of few-layer Li_2S_2 (4 block layers) located on the different substrates of $Ti_3C_2T_2$ (T= H, O, F, S, Cl, Se, Te, Br, OH, and NH).

Note 3:

It was found that the few-layer Li_2S_2 and Li_2S will become stable while their block layers are increased to 4 and 3 (see Figure S6), respectively. Therefore, the heterojunctions were built from the stable few-layer Li_2S_2 and Li_2S, and the different functionalized surfaces with a vacuum layer of 15 Å.

The formation energy E_f for a Li_2S-heterojunction can be expressed as:

$$E_f = \left(E_{heterojunction} - E_{Ti_3C_2T_2} - E_{Few-layer\ Li_2S} \right)/n$$

where $E_{heterojunction}$, $E_{Ti_3C_2T_2}$, and $E_{Few-layer\ Li_2S}$ represent the total energies of heterojunction, functionalized $Ti_3C_2T_x$, and few-layer Li_2S (3 block layers), respectively. n (n=12) is the number of Li_2S units.

Table S3 Calculated values of $E_{heterojunction}$, $E_{Ti_3C_2T_2}$, $E_{Few-layer\ Li_2S}$ and E_f based on the heterojunction models of $Ti_3C_2T_x$ -(few-layer) Li_2S_2 (T=H, O, F, S, Cl, Se, Br, OH, and NH)

eV	$Ti_3C_2H_2$	$Ti_3C_2O_2$	$Ti_3C_2F_2$	$Ti_3C_2S_2$	$Ti_3C_2Cl_2$
$E_{heterojunction}$	-634.05	-730.51	-681.54	-645.61	-630.53
$E_{Ti_3C_2T_2}$	-493.44	-589.44	-542.75	-528.91	-501.00
$E_{Few-layer\ Li_2S}$	-148.20	-148.20	-148.20	-148.20	-148.20
E_f(eV/f.u.)	0.63	0.59	0.78	2.62	1.55
eV	$Ti_3C_2Se_2$	$Ti_3C_2Br_2$	$Ti_3C_2Te_2$	$Ti_3C_2(OH)_2$	$Ti_3C_2(NH)_2$
$E_{heterojunction}$	-662.48	-608.86	-625.72	-790.93	-808.72
$E_{Ti_3C_2T_2}$	-513.12	-481.57	-492.39	-649.07	-667.14
$E_{Few-layer\ Li_2S}$	-148.20	-148.20	-148.20	-148.20	-148.20
E_f(eV/f.u.)	-0.09	1.74	1.24	0.53	0.55