Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information for

Nitride MXenes as sulfur hosts for thermodynamic and kinetic suppression of polysulfide shuttling: a computational study

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Additional computational methods

The adsorption energy E_{ad} of Li_2S_n (S_8) on the V_2N/V_2NT_2 monolayers was calculated based on the following equation:

$$E_{ad} = E_{MXene + Li_2S_n(S_8)} - E_{MXene} - E_{Li_2S_n(S_8)} \quad (1)$$

where E_{MXene} and $E_{MXene + Li_2S_n(S_8)}$ are the total energy of V_2N/V_2NT_2 before and after adsorption with Li_2S_n (S_8), and $E_{Li_2S_n(S_8)}$ is the total energy of Li_2S_n (S_8).

The differential charge density as a function of space was obtained as the difference between the valence charge density before and after the bonding:

$$\Delta\rho(\vec{r}) = \rho_{MXene + Li_2S_n(S_8)}(\vec{r}) - \rho_{MXene}(\vec{r}) - \rho_{Li_2S_n(S_8)}(\vec{r}) \quad (2)$$

where $\rho_{MXene + Li_2S_n(S_8)}(\vec{r})$, $\rho_{Mxene}(\vec{r})$, and $\rho_{Li_2S_n(S_8)}(\vec{r})$ represent the charge density distributions of $Li_2S_n(S_8)$-adsorbed on V_2N/V_2NT_2 systems, bare V_2N/V_2NT_2 monolayer, and $Li_2S_n(S_8)$ molecule respectively.

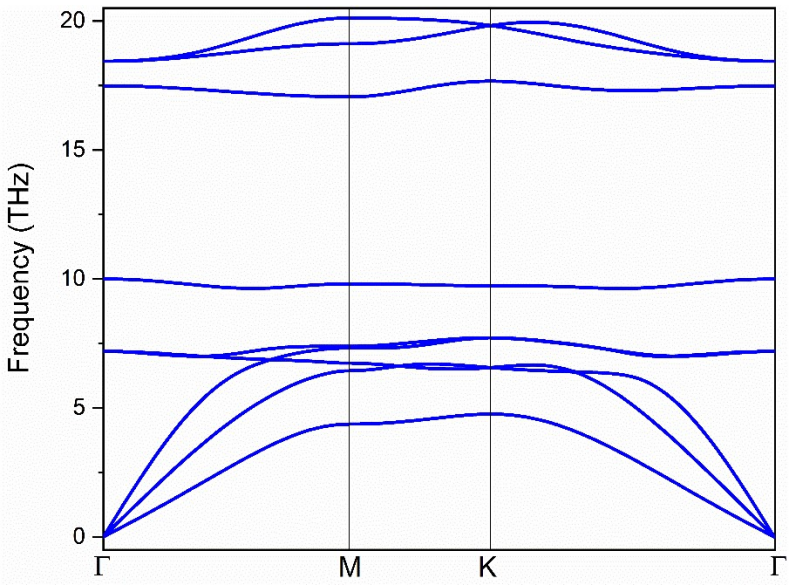


Fig. S1 Phonon dispersion spectra of V_2N.

Table S1. DFT-calculated total energies of the three sites for different terminating groups T (see Fig. 1b) in V_2NT_2 phases.

	V_2NO_2 (eV)	V_2NF_2 (eV)	$V_2N(OH)_2$ (eV)	V_2NS_2 (eV)
α	-444.42	-441.09	-447.56	-442.43
β	-442.81	-440.42	-446.35	-440.68
γ	-443.86	-440.72	-447.21	-442.08

Table S2. The lattice constants *a*, *b* and V-N bond length (in Å) in V_2N and V_2NT_2.

	V_2N	V_2NO_2	V_2NF_2	$V_2N(OH)_2$	V_2NS_2
a, *b*	2.89	2.90	3.04	3.04	3.07
V(1)-N	1.97	2.04	1.99	2.00	2.06
V(1)-T	-	1.95	2.15	2.14	2.36

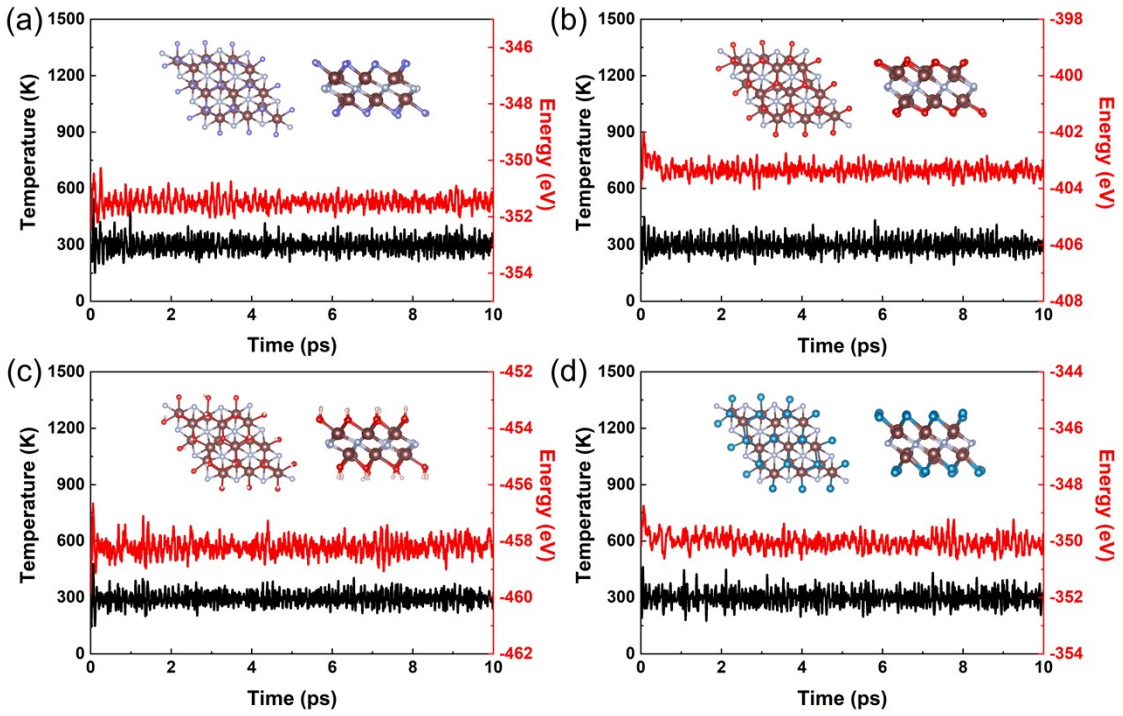


Fig. S2 Temperature and total energy as a function of time for (a) V_2NF_2, (b) V_2NO_2, (c) $V_2N(OH)_2$, and (d) V_2NS_2 during the AIMD simulation (inset: the structure after 10 ps AIMD simulation. V, N, F, O, H, and S atoms are represented in brown, grey, purple, red, pink, and blue, respectively).

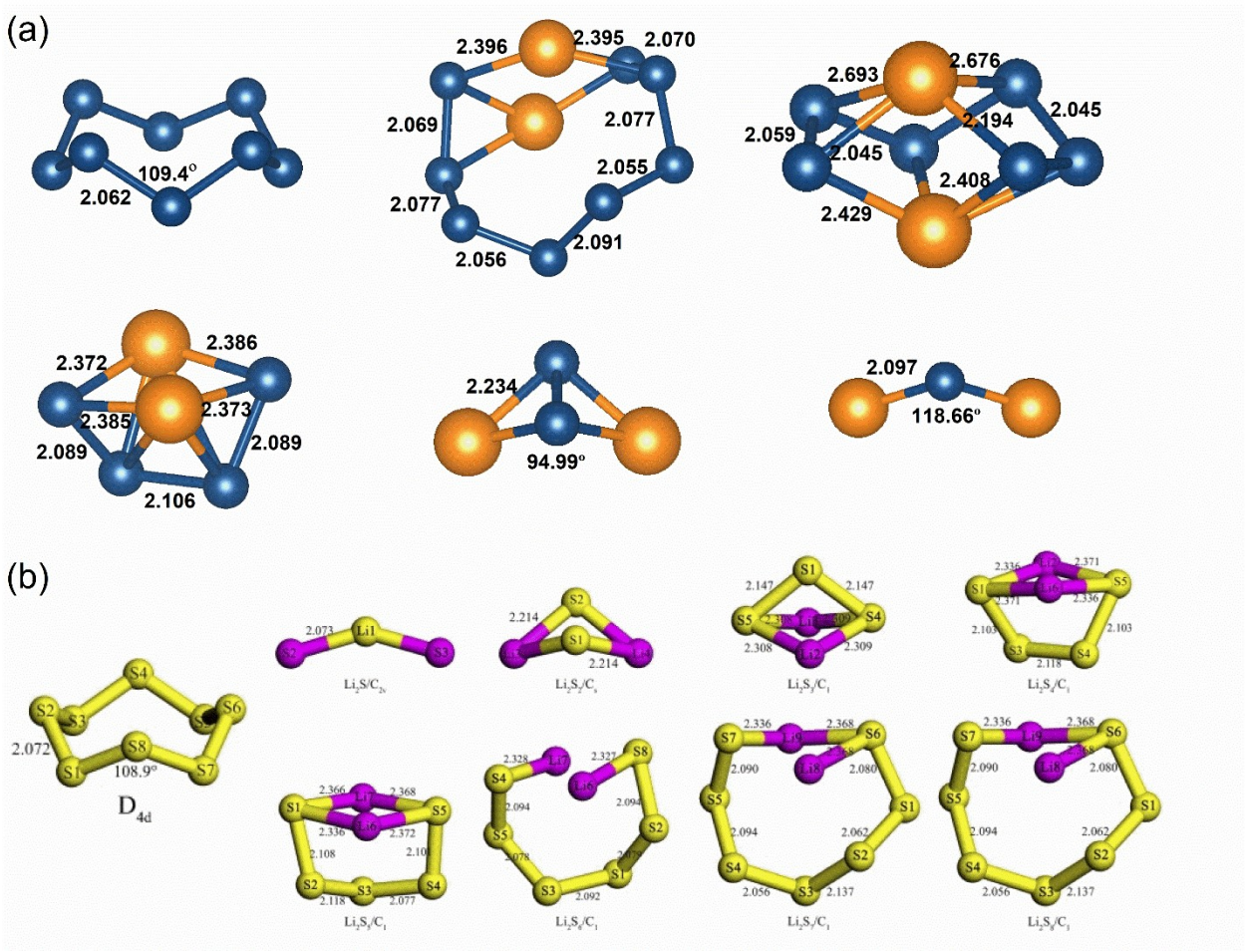
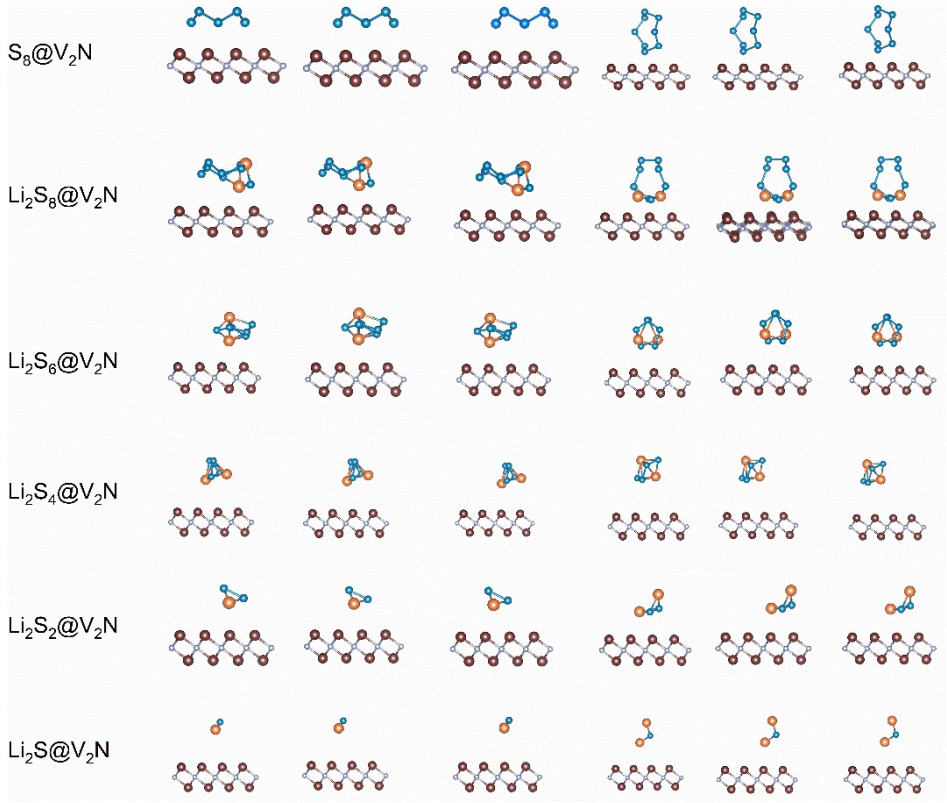
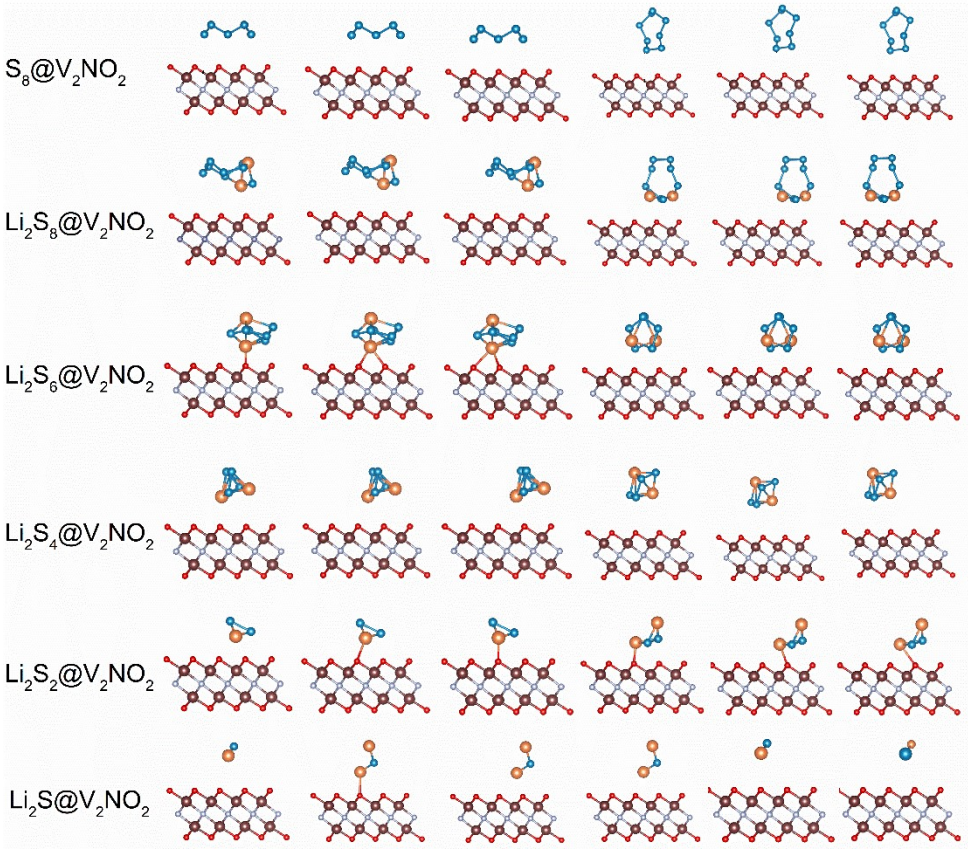
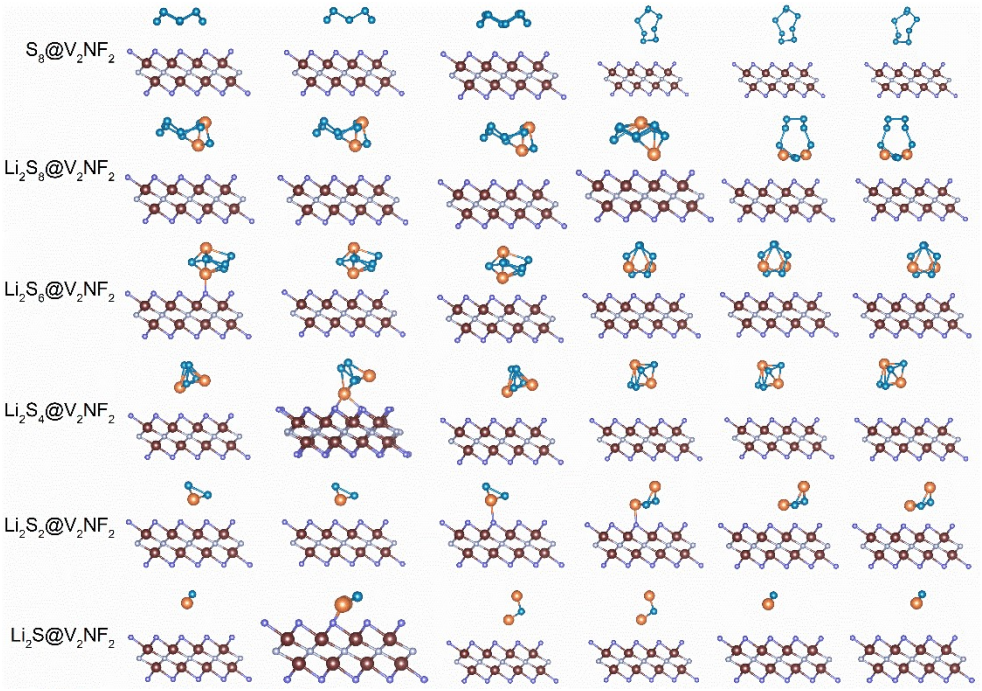
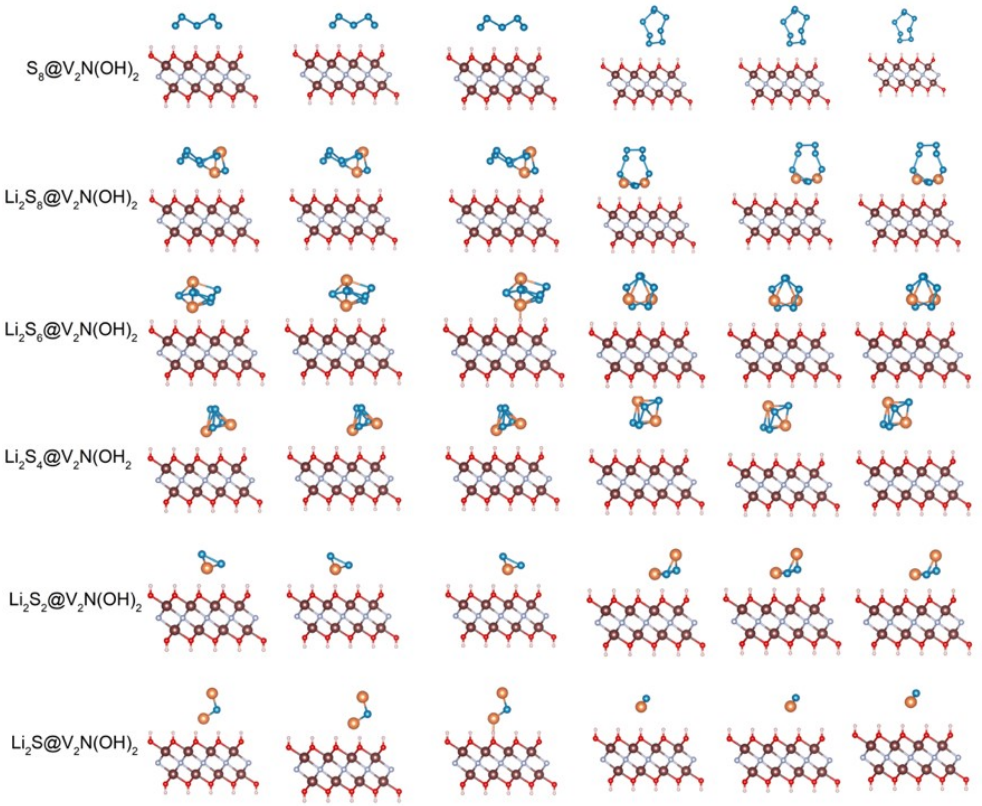


Fig. S3 (a) Optimized geometries of S_8 and Li_2S_n (n = 1, 2, 4, 6, and 8) with bond lengths (in Å) and angles labeled in the figure and (b) the comparison with their most stable structures in ref. 1 obtained by using B3LYP/6-311G(3df)-level quantum chemistry calculations.


$S_8@V_2N$
$Li_2S_8@V_2N$
$Li_2S_6@V_2N$
$Li_2S_4@V_2N$
$Li_2S_2@V_2N$
$Li_2S@V_2N$


$S_8@V_2NO_2$
$Li_2S_8@V_2NO_2$
$Li_2S_6@V_2NO_2$
$Li_2S_4@V_2NO_2$
$Li_2S_2@V_2NO_2$
$Li_2S@V_2NO_2$


$S_8@V_2NF_2$
$Li_2S_8@V_2NF_2$
$Li_2S_6@V_2NF_2$
$Li_2S_4@V_2NF_2$
$Li_2S_2@V_2NF_2$
$Li_2S@V_2NF_2$


$S_8@V_2N(OH)_2$
$Li_2S_8@V_2N(OH)_2$
$Li_2S_6@V_2N(OH)_2$
$Li_2S_4@V_2N(OH_2$
$Li_2S_2@V_2N(OH)_2$
$Li_2S@V_2N(OH)_2$

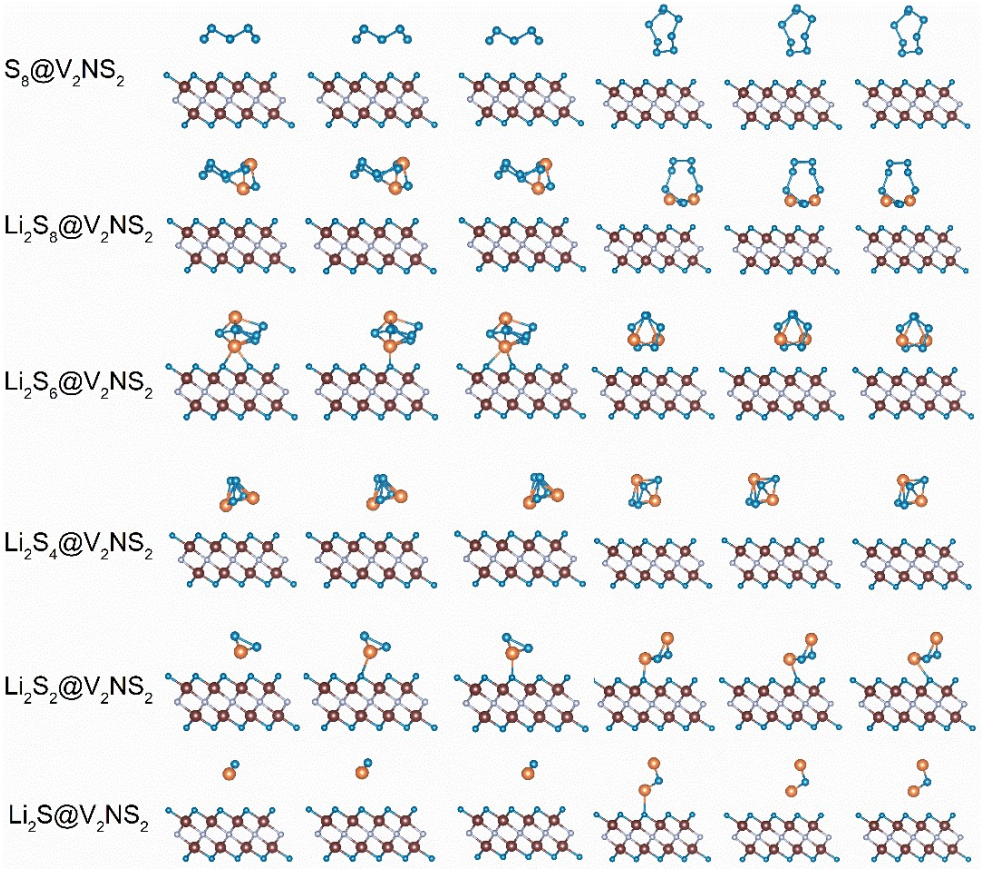


Fig. S4 A total number of 180 different adsorption configurations of S_8 and Li_2S_n on the surface of V_2N, V_2NO_2, V_2NF_2, $V_2N(OH)_2$, and V_2NS_2. The V, N, O, F, H, Li, and S atoms are distinguished by brown, gray, red, purple, pink, orange, and blue color, respectively.

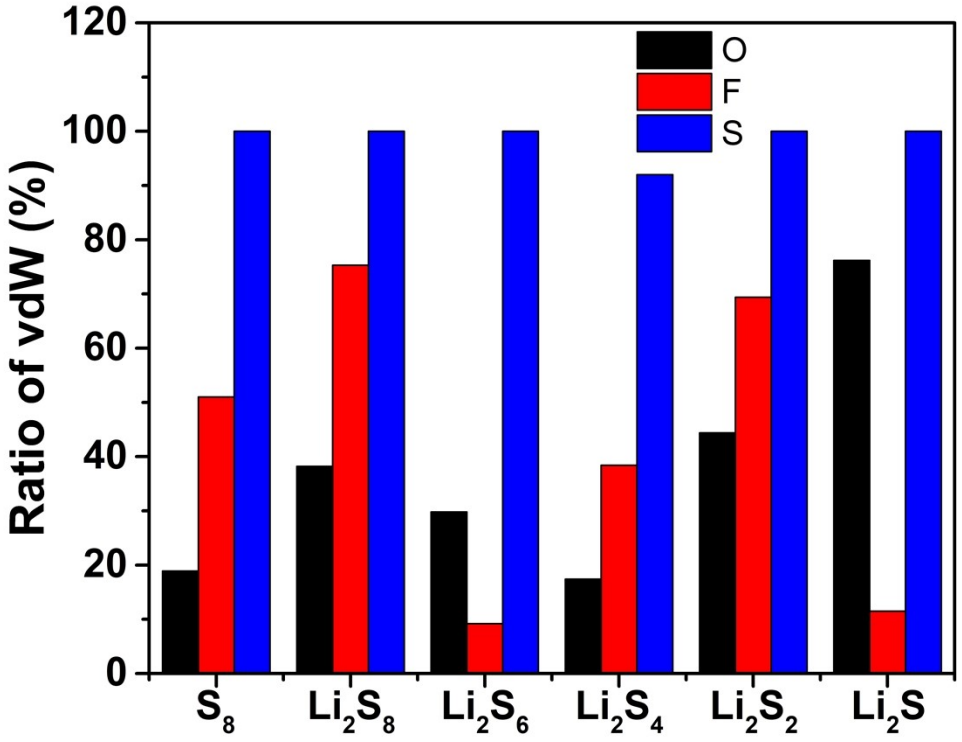


Fig. S5 Ratio of vdW (R_{vdW}) interaction of S_8 and Li_2S_n on V_2NO_2, V_2NF_2, and V_2NS_2.

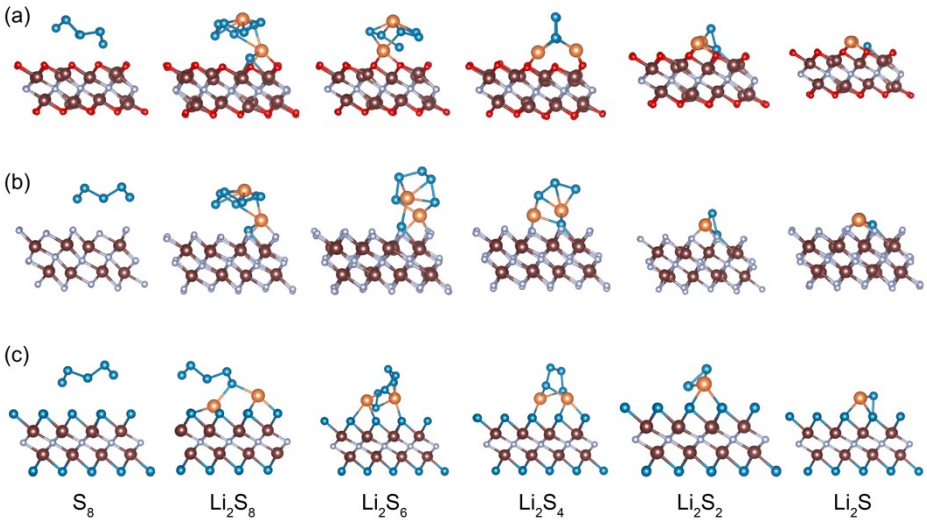


Fig. S6 The optimized structure of S_8 and Li_2S_n on the surface of (a) V_2NO_{2-x}, (b) V_2NF_{2-x}, and (c) V_2NS_{2-x} (x = 1/16). The V, N, O, F, Li, and S atoms are distinguished by brown, gray, red, purple, orange, and blue color, respectively.

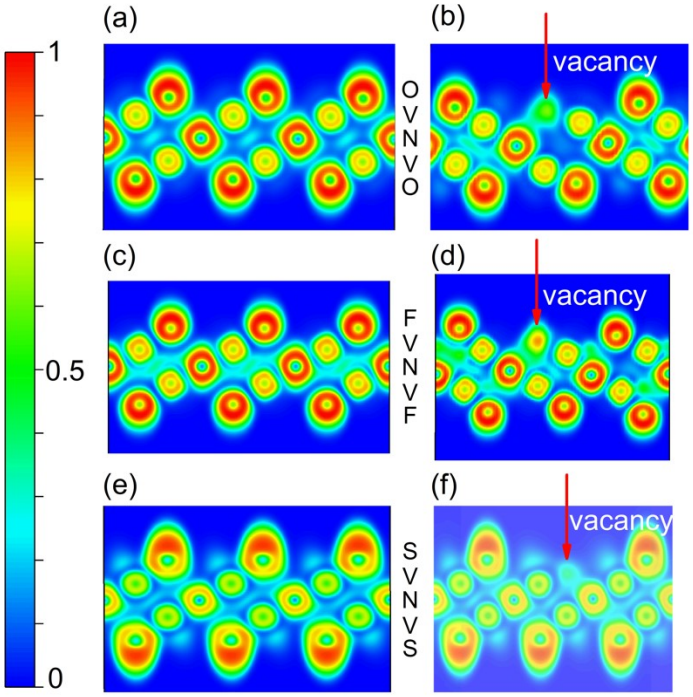


Fig. S7 Electron localization functions (ELF) of the (110) slice of (a) V_2NO_2; (b) V_2NO_{2-x}; (c) V_2NF_2; (d) V_2NF_{2-x}; (e) V_2NS_2; (f) V_2NS_{2-x}. The scale bar shows the isodensity values of ELF. The values of 1.00 and 0.50 correspond to fully localized and fully delocalized electrons, respectively, while the value 0.00 refers to very low charge density.

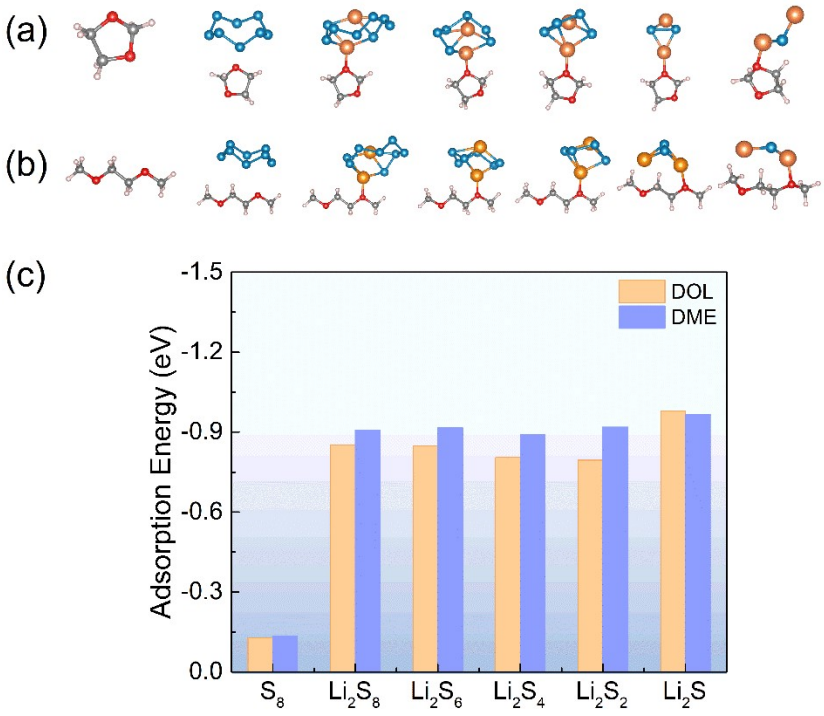


Fig. S8 Configurations of S_8 and Li_2S_n bonding with (a) DOL and (b) DME. (c) Adsorption energies of S_8 and Li_2S_n with DOL and DME.

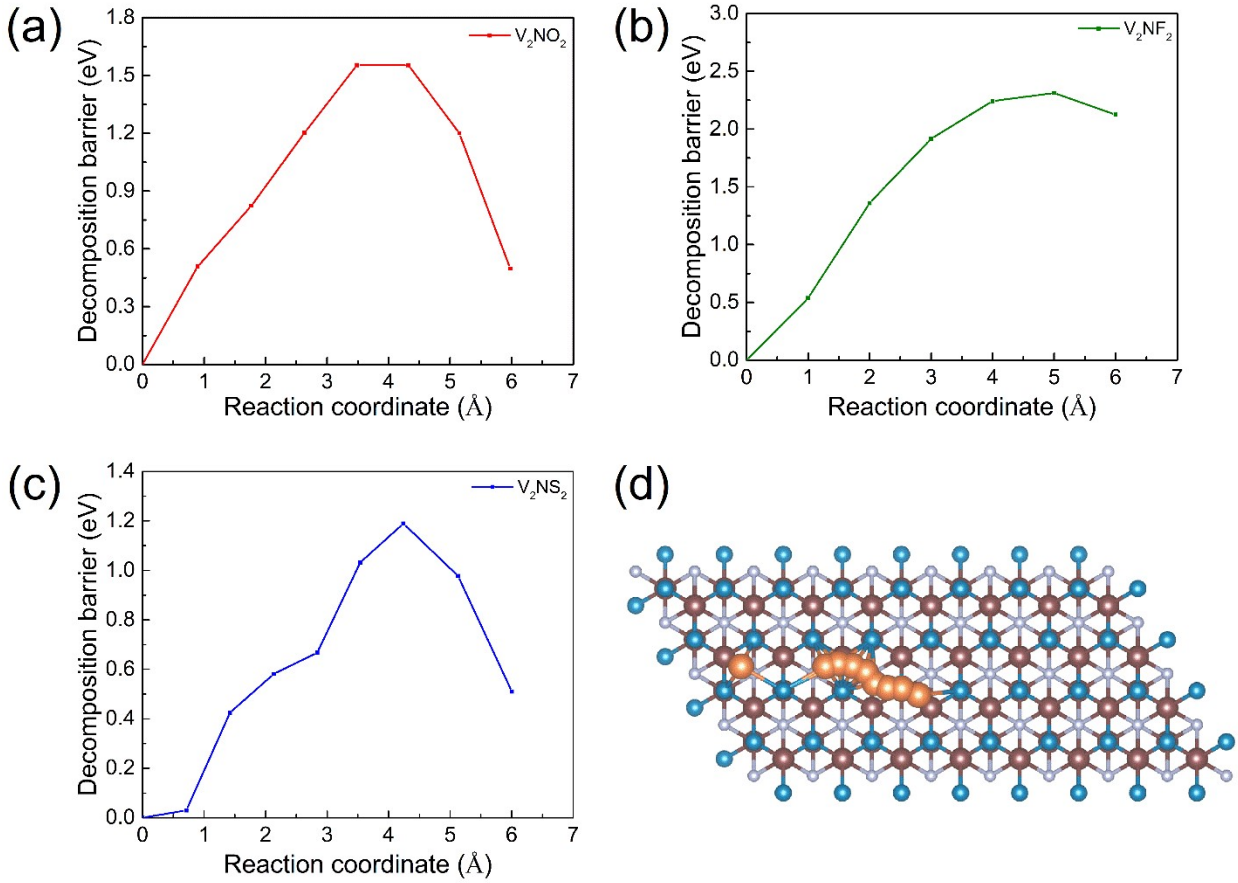


Fig. S9 Energy profiles for Li_2S decomposition on 8×4×1 supercells of (a) V_2NO_2, (b) V_2NF_2, and (c) V_2NS_2, and (d) illustration of intermediate structures during Li_2S decomposition on V_2NS_2 surface through the favorable pathway as an example. The V, N, S, and Li atoms are distinguished by brown, gray, blue, and orange color, respectively.

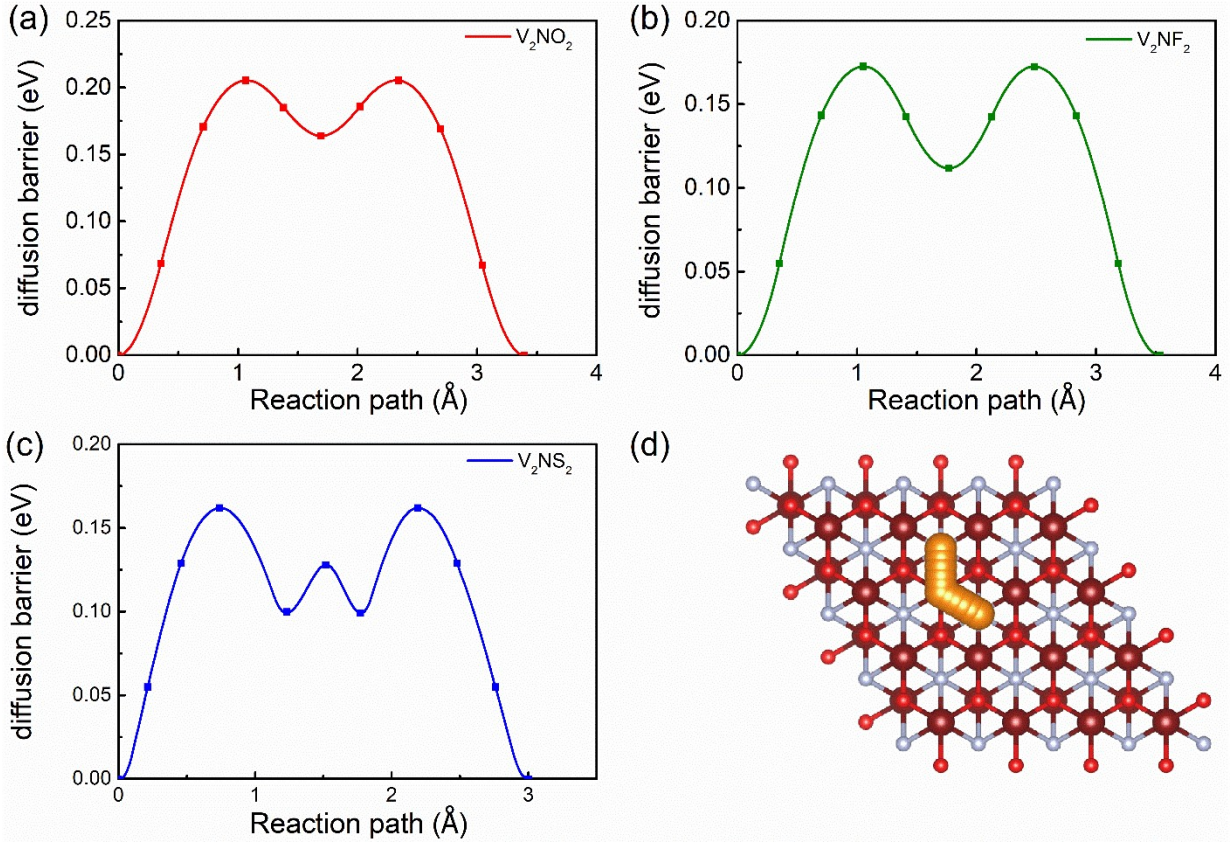


Fig. S10 Energy profiles for Li^+ diffusion on (a) V_2NO_2, (b) V_2NF_2 and (c) V_2NS_2, and (d) illustration of the diffusion of single Li atom over surface through the favorable pathway. The V, N, O and Li atoms are distinguished by brown, gray, red, and orange color, respectively.

Table S3. Li^+ diffusion barriers on V_2NT_2 and other MXenes reported in literature.

System	Li^+ diffusion barrier (eV)	Reference
V_2NO_2	0.21	This work
V_2NF_2	0.17	This work
V_2NS_2	0.16	This work
V_2CS_2	0.17	[2]
V_2CO_2	0.26	[2]
V_2C	0.19	[2]
$Ti_3C_2O_2$	0.236	[3]
$Ti_3C_2S_2$	0.188	[3]
$Ti_3C_2F_2$	0.187	[3]
$Ti_3C_2Cl_2$	0.196	[3]
Ti_2NS_2	0.19	[4]
V_2NS_2	0.17	[4]
Ti_3CNF_2	0.24	[5]
Ti_3CNO_2	0.26	[5]

Supplementary References

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