Supporting Information

Metallic C_5N Monolayer as Efficient Catalyst for Accelerating Redox Kinetics of Sulfur in Lithium-Sulfur Batteries

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Note1.Computational details

The adsorption energy (E_{ads}) of adsorbates were obtained by following formula:

$$E_{ads} = E_{total} - E_{substrate} - E_{adsorbate} \quad (1)$$

where E_{total}, $E_{substrate}$ and $E_{adsorbate}$ denoted the total energy of adsorbed system, substrate, and isolated adsorbate, respectively. Considering the definition, the lower the E_{ads}, the stronger the interaction between the substrate and adsorbate is.

The cohesive energy (E_{coh}) of both phases C_5N is calculated by $E_{coh} = (E_{C5N} - 5E_C - E_N)/6$, where E_{C5N}, E_C and E_N are the energy of C_5N per formula, energies of isolated C and N atoms, respectively, and 6 represents the total number of atoms in C_5N formula.

The Gibbs free energy of Li_2S_n and S_8 are calculated by

$$G = E_{DFT} + E_{ZPE} - TS \quad (2)$$

where E_{DFT}, E_{ZPE}, and S stand for the total energy obtained by DFT simulation, zero-point energy, and the entropy, respectively. The zero-point energies of LiPs and S_8 cluster were obtained from vibrational frequency calculations and could be determined as ZPE = $\frac{1}{2}\Sigma_i h\nu_i$, here h and ν_i are Planck constant and vibrational frequencies, respectively. T is the standard room temperature (298.15 K).

The elementary reaction steps for sulfur reduction[1] are considered as:

$$S_8 + 16Li^+ \rightarrow S_8^* + 16Li^+ \quad \#(3)$$

$$S_8^* + 16Li^+ + 2e^- \rightarrow Li_2S_8^* + 14Li^+ \quad \#(4)$$

$$Li_2S_8^* + 14Li^+ + 2e^- \rightarrow Li_2S_6^* + Li_2S_2 + 12Li^+ \quad \#(5)$$

$$Li_2S_6^* + Li_2S_2 + 12Li^+ + 2e^- \rightarrow Li_2S_4^* + 2Li_2S_2 + 10Li^+ \quad \#(6)$$

$$Li_2S_4^* + 2Li_2S_2 + 10Li^+ + 2e^- \rightarrow Li_2S_2^* + 3Li_2S_2 + 8Li^+ \quad \#(7)$$

$$Li_2S_2^* + 3Li_2S_2 + 8Li^+ + 8e^- \rightarrow Li_2S^* + 7Li_2S \#(8)$$

The energy of a single Li ion and an electron ($Li^+ + e^-$) pair was treated as the energy of a single Li atom from its crystalline phase. The adsorbate with an asterisk "*" refers to the state of being adsorbed, whereas the isolated state does not have a star mark.

Table S1. The k-meshes used for different types of calculations related to H-C_5N.

k-point	structural relaxation	Self-consistent field	Density of states
Primitive cell	7×7×1	11×11×1	13×13×1
Super cell	2×2×1	5×5×1	-
Nanoribbon	1×9×1	1×15×1	1×15×1

Table S2. The k-meshes used for different types of calculations related to O-C_5N.

k-mesh	structural relaxation	Self-consistent field	Density of states
Primitive cell	5×25×1	5×25×1	6×30×1
Super cell	2×6×1	3×9×1	-
Nanoribbon	6×1×1	8×1×1	10×1×1

Data1. For Section 3.1

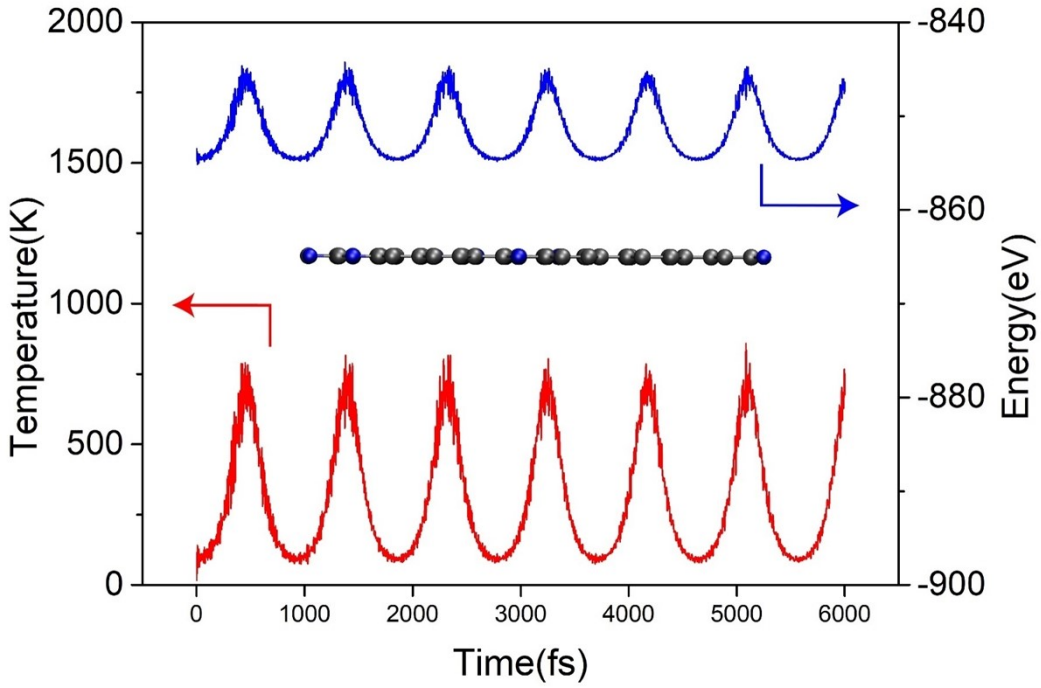

Fig. S1. Variations of temperature and energy against time for MD simulations of the H-C_5N monolayer, and the inset shows the side view of the snapshot of the atomic configuration. The simulation is run at 300 K for 6 ps with a time step of 3 fs.

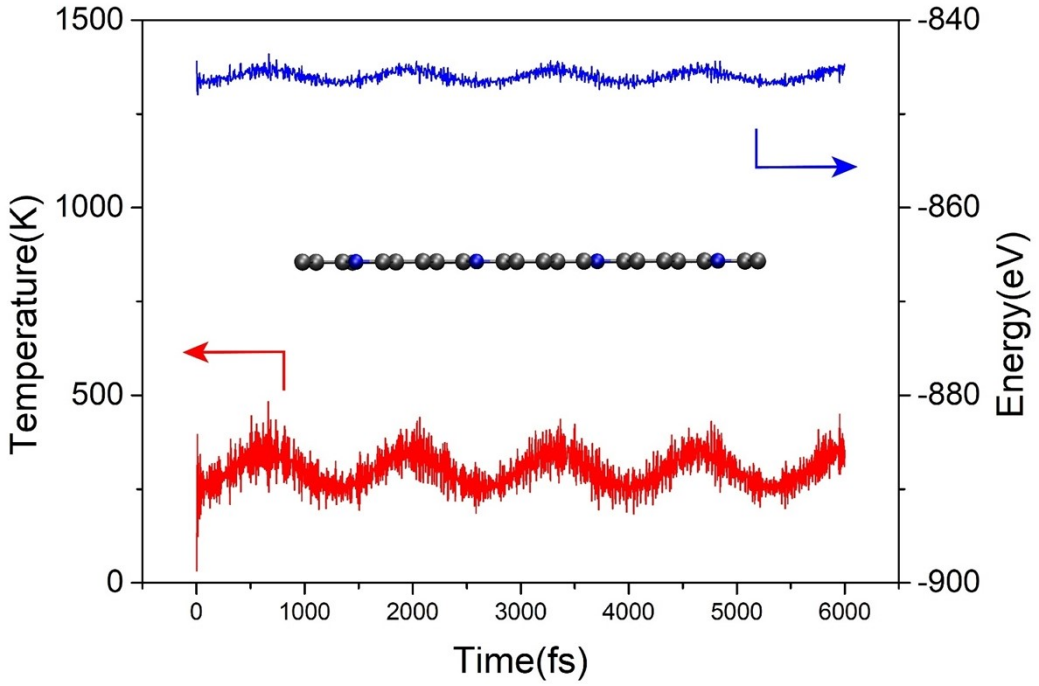

Fig. S2. Variations of temperature and energy against time for MD simulations of the O-C_5N monolayer, and the inset shows the side view of the snapshot of the atomic configuration. The simulation is run at 300 K for 6 ps with a time step of 3 fs.

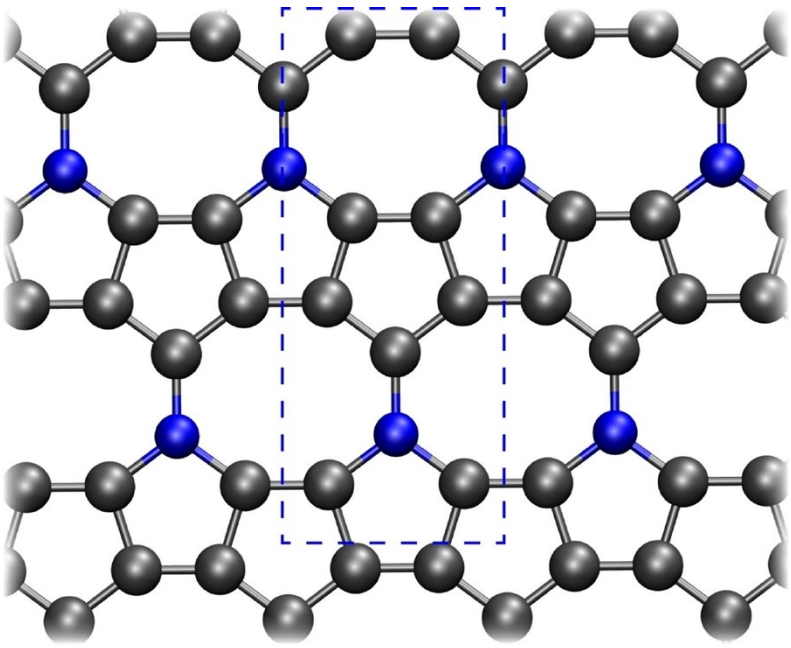

Fig. S3. Fully relaxed C_5N with another atomic arrangement from the literature[2]. Our simulation results give rise to the lattice constants of a = 3.66 Å and b = 8.88 Å and the cohesive energy of -7.20 eV for this configuration, which are in accordance with the previous report.

Table S3. The charge transfers between adsorbates and O-C_5N. The positive value means the charge transfer from adsorbates to O-C_5N and the negative value represent the reverse direction of charge transfer.

LiPs	charge transfer/e
Li_2S	-1.147
Li_2S_2	0.218
Li_2S_4	0.027
Li_2S_6	0.015
Li_2S_8	0.008
S_8	-0.050

Data2. For Section 3.2

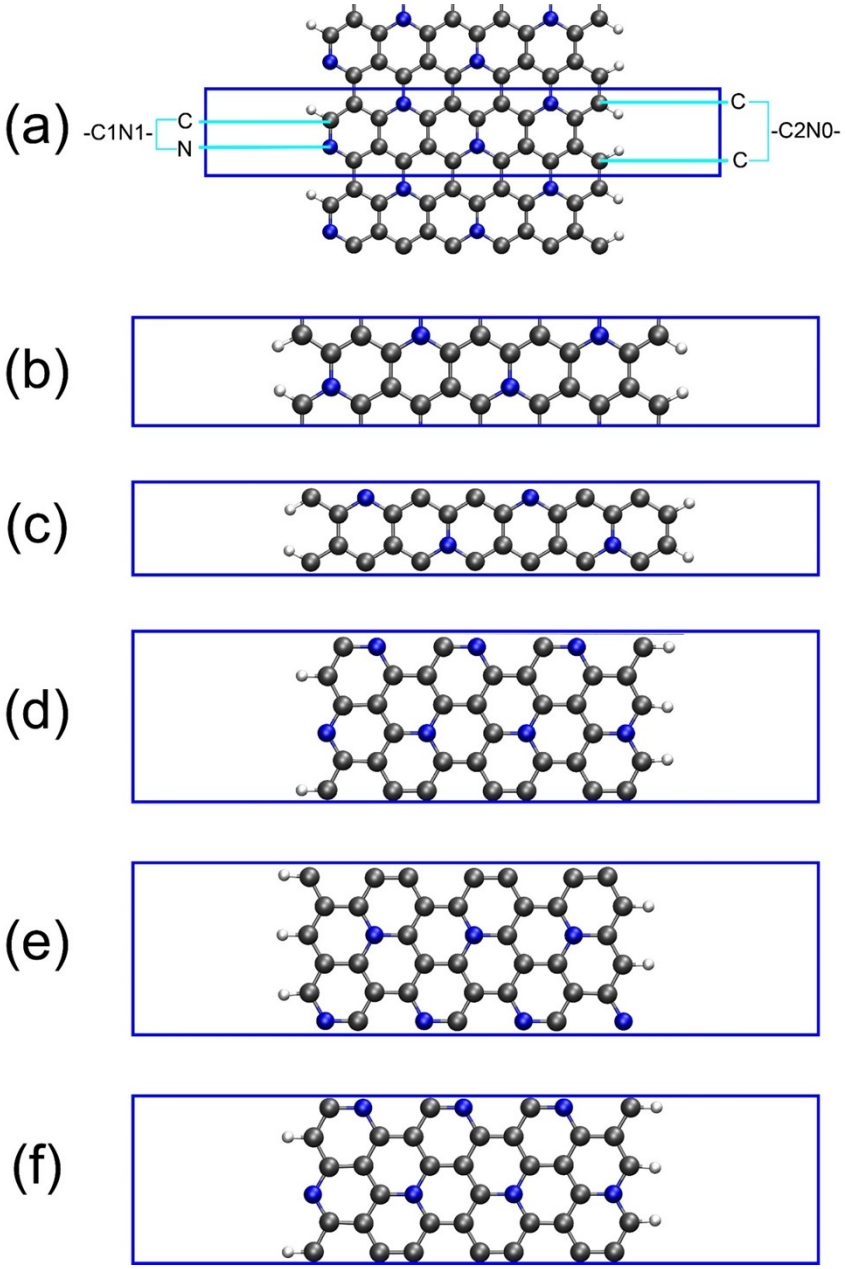

Fig. S4. Optimized structures of H-A-C1N1-C2N0 (a), H-A-C2N0-C2N0-1 (b), H-A-C2N0-C2N0-2 (c), H-Z-C2N1-C3N0-1 (d), H-Z-C3N0-C2N1 (e), H-Z-C2N1-C3N0-2 (f). We use -1/-2 to identify the two nanoribbons terminated with the same types of edge atoms but with different atomic arrangements. Taking H-A-C1N1-C2N0 (a) as example, it denotes the nanoribbon with armchair edges derived from H-C_5N with successive edge atoms of one C atom and one N atom at the left side and two C atoms and single N atom at the right side of the ribbon, respectively. **In general, H-A- C*m*N*n*-C*p*N*q* (*m*, *n*, *p and q* = integer) denotes that there exist *m* C atoms and *n* N atoms at left side and *p* C atoms and *q* N atoms at right side of the ribbon with armchair edge obtained from the H-C_5N.**

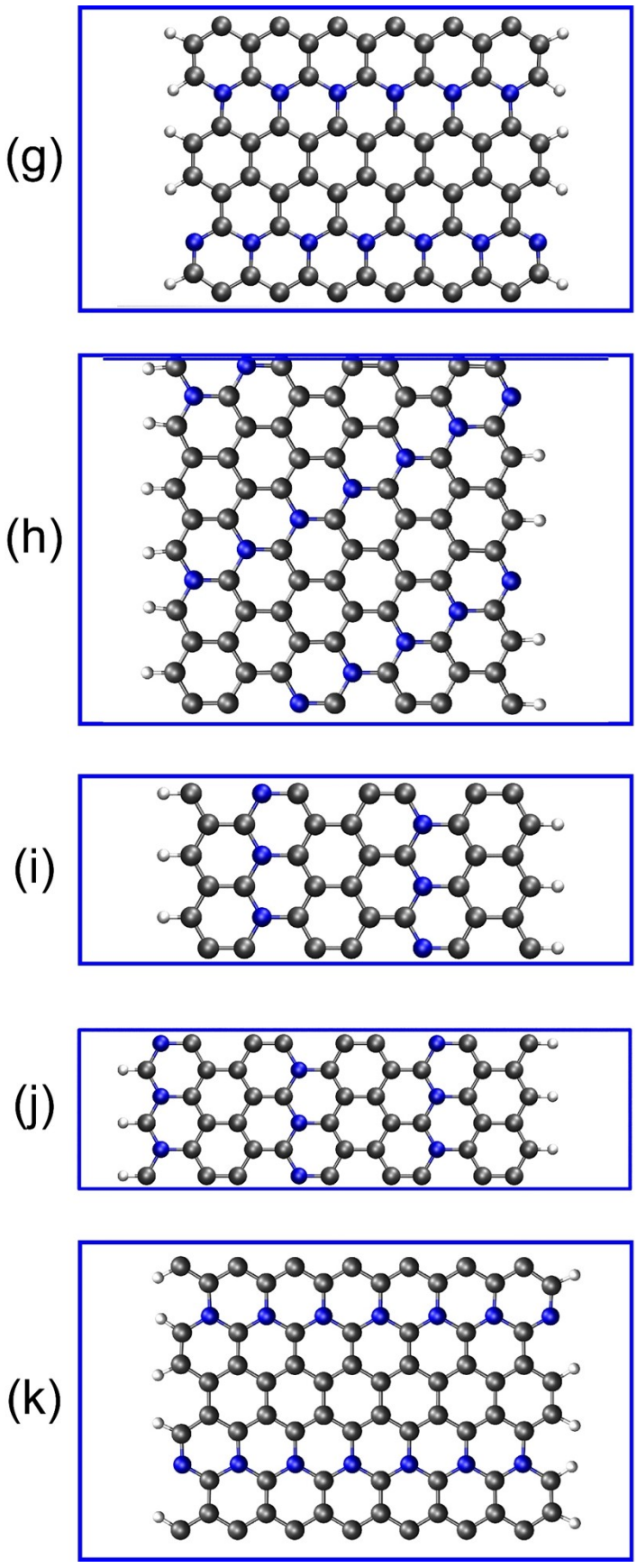

Fig. S5. Optimized structures of O-A-C5N1-C5N1-1 (g), O-Z-C6N0-C4N2 (h), O-Z-C3N0-C3N0-1 (i), O-Z-C3N0-C3N0-2 (j) and O-A-C5N1-C5N1-2 (k).

Table S4. Adsorption energies of Li_2S_6 on different nanoribbons. Bolded C*m*N*n* present the situation that LiPs adsorb on that side of nanoribbon.

Different Nanoribbon	E_{ads}/eV
H-A-**C2N0**-C2N0-1	-0.64
H-A-C2N0-**C2N0**-1	-0.76
H-A-**C2N0**-C2N0-2	-0.83
H-A-C2N0-**C2N0**-2	-0.81
H-Z-**C2N1**-C3N0-1	-0.23
H-Z-C2N1-**C3N0**-1	-0.22
H-Z-**C2N1-C3N0**-2	-0.23
O-A-C5N1-**C5N1**-1	-0.60
H-Z-**C3N0**-C2N1	-0.21
H-Z-C3N0-**C2N1**	-0.46
O-Z-**C6N0**-C4N2	-0.39
O-Z-C6N0-**C4N2**	-0.49
O-Z-**C3N0**-C3N0-1	-0.71
O-Z-C3N0-**C3N0**-1	-0.73
O-Z-**C3N0**-C3N0-2	-0.87
O-Z-C3N0-**C3N0**-2	-0.76
O-A-**C5N1**-C5N1-2	-0.74
H-A-**C1N1**-C2N0	-1.03
H-A-C1N1-**C1N1**	-1.07
O-Z-C2N0-**C0N2**	-1.72

Table S5. The variation in bond length (Δd) and bond angle (ΔA) after LiPs adsorbed on O-Z-C2N0-**C0N2** nanoribbon. Herein, the variations are calculated as the difference between that of adsorbed LiPs and isolated LiPs. The subscripts, Li-S, S-S and Li-S-Li, in $\Delta d_{Li\text{-}S}$, $\Delta d_{S\text{-}S}$ and $\Delta A_{Li\text{-}S\text{-}Li}$ stand for Li-S and S-S bonds as well as Li-S-Li angle in Li_2S, respectively.

LiPs	$\Delta d_{Li\text{-}S}$(Å)	$\Delta d_{S\text{-}S}$(Å)	$\Delta A_{Li\text{-}S\text{-}Li}$(°)
Li_2S	0.25	-	44.34
Li_2S_2	0.27	0.23	-
Li_2S_4	0.16	0.04	-
Li_2S_6	-0.05	0.01	-
Li_2S_8	0.03	0.02	-
S_8	-	0.00	-

Table S6. The variations in bond length and bond angle after LiPs adsorbed on H-A-**C1N1**-C2N0.

LiPs	$\Delta d_{Li\text{-}S}$(Å)	$\Delta d_{S\text{-}S}$(Å)	$\Delta A_{Li\text{-}S\text{-}Li}$(°)
Li_2S	0.17	-	13.37
Li_2S_2	0.02	-0.10	-
Li_2S_4	0.12	-0.01	-
Li_2S_6	0.00	-0.01	-
Li_2S_8	-0.02	0.00	-
S_8	-	0.00	-

Table S7. The variations in bond length and bond angle after LiPs adsorbed on H-A-C1N1-**C1N1**.

LiPs	$\Delta d_{Li\text{-}S}$(Å)	$\Delta d_{S\text{-}S}$(Å)	$\Delta A_{Li\text{-}S\text{-}Li}$(°)
Li_2S	0.16	-	9.41
Li_2S_2	0.08	-0.11	-
Li_2S_4	0.12	-0.01	-
$L_{i2}S_6$	0.10	-0.01	-
Li_2S_8	-0.03	-0.01	-
S_8	-	0.00	-

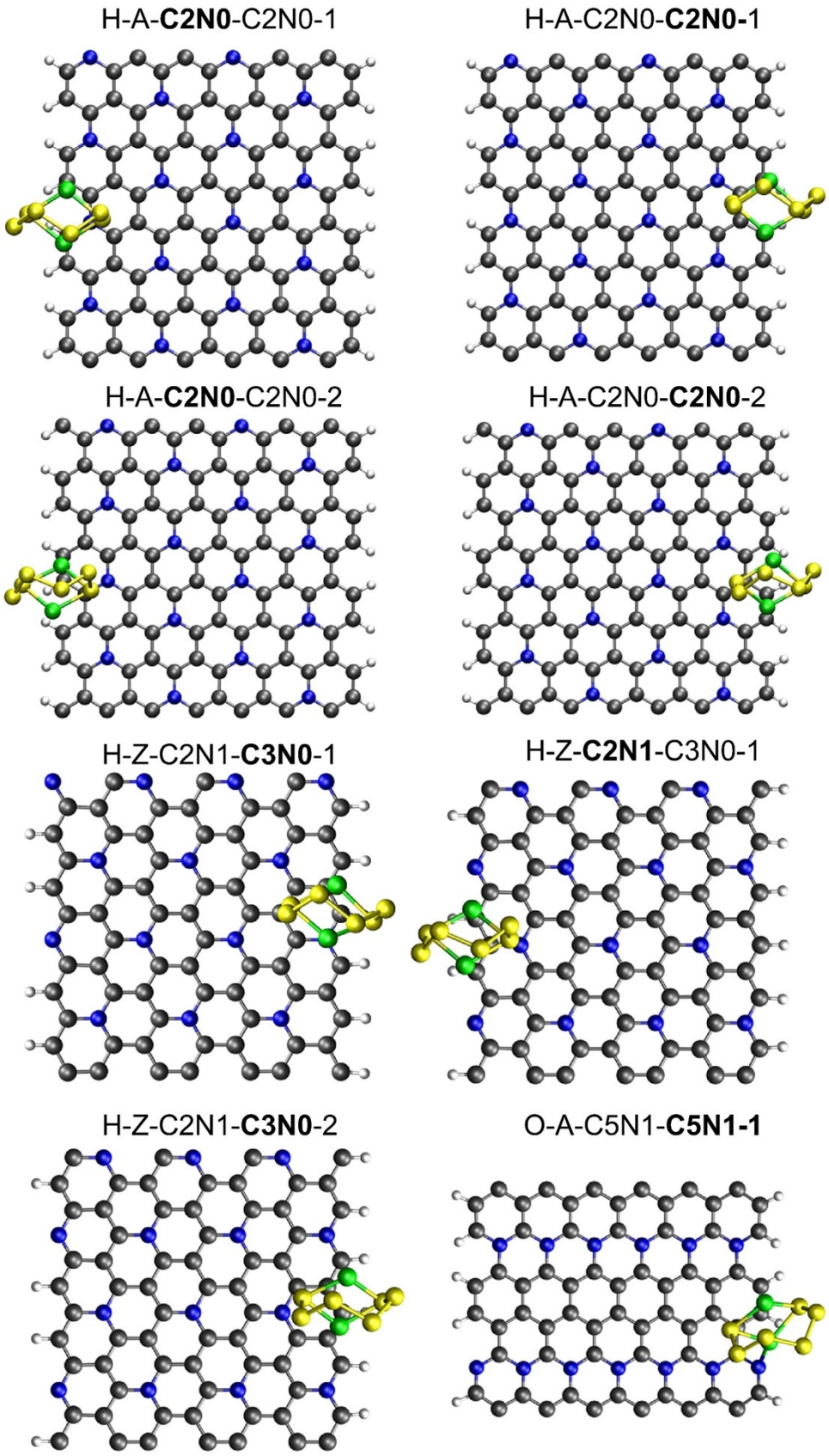

Fig. S6. Optimized structures of Li_2S_6 adsorbed on the five kinds of nanoribbons.

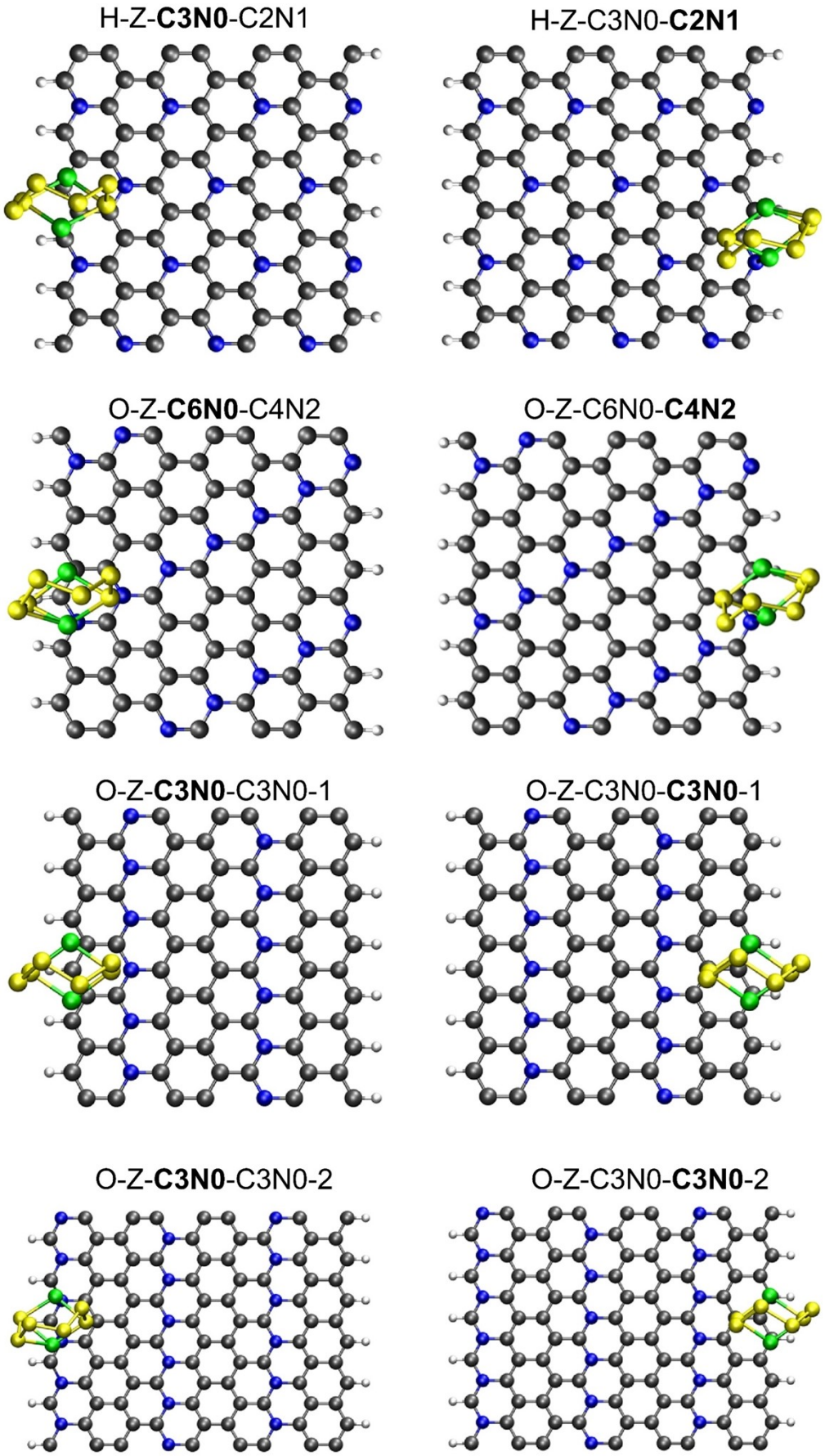

Fig. S7. Optimized structures of Li_2S_6 adsorbed on the four kinds of nanoribbons.

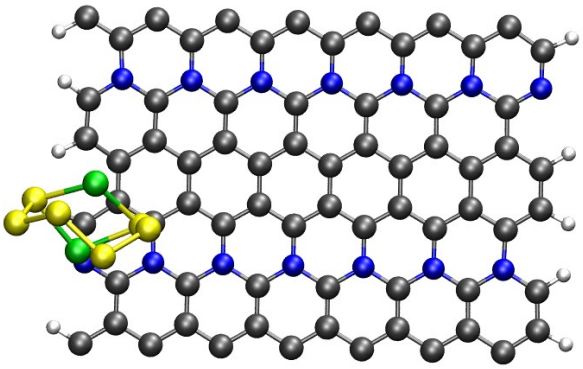

Fig. S8. Optimized structure of Li_2S_6 adsorbed on the O-A-**C5N1**-C5N1-2 nanoribbon.

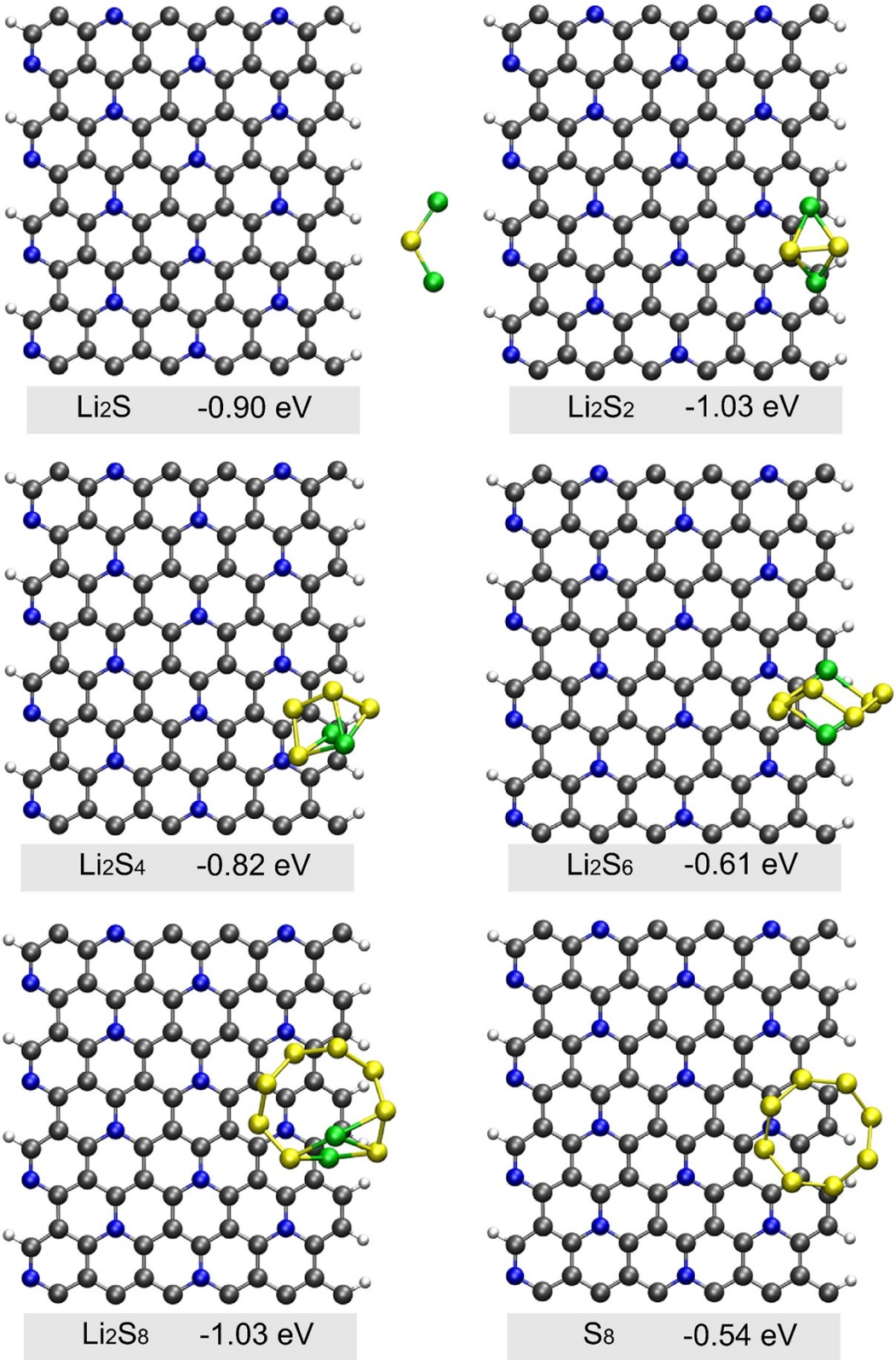

Fig. S9. Optimized structures of LiPs adsorbed on the H-A-C1N1-**C2N0** nanoribbon, and corresponding E_{ads}.

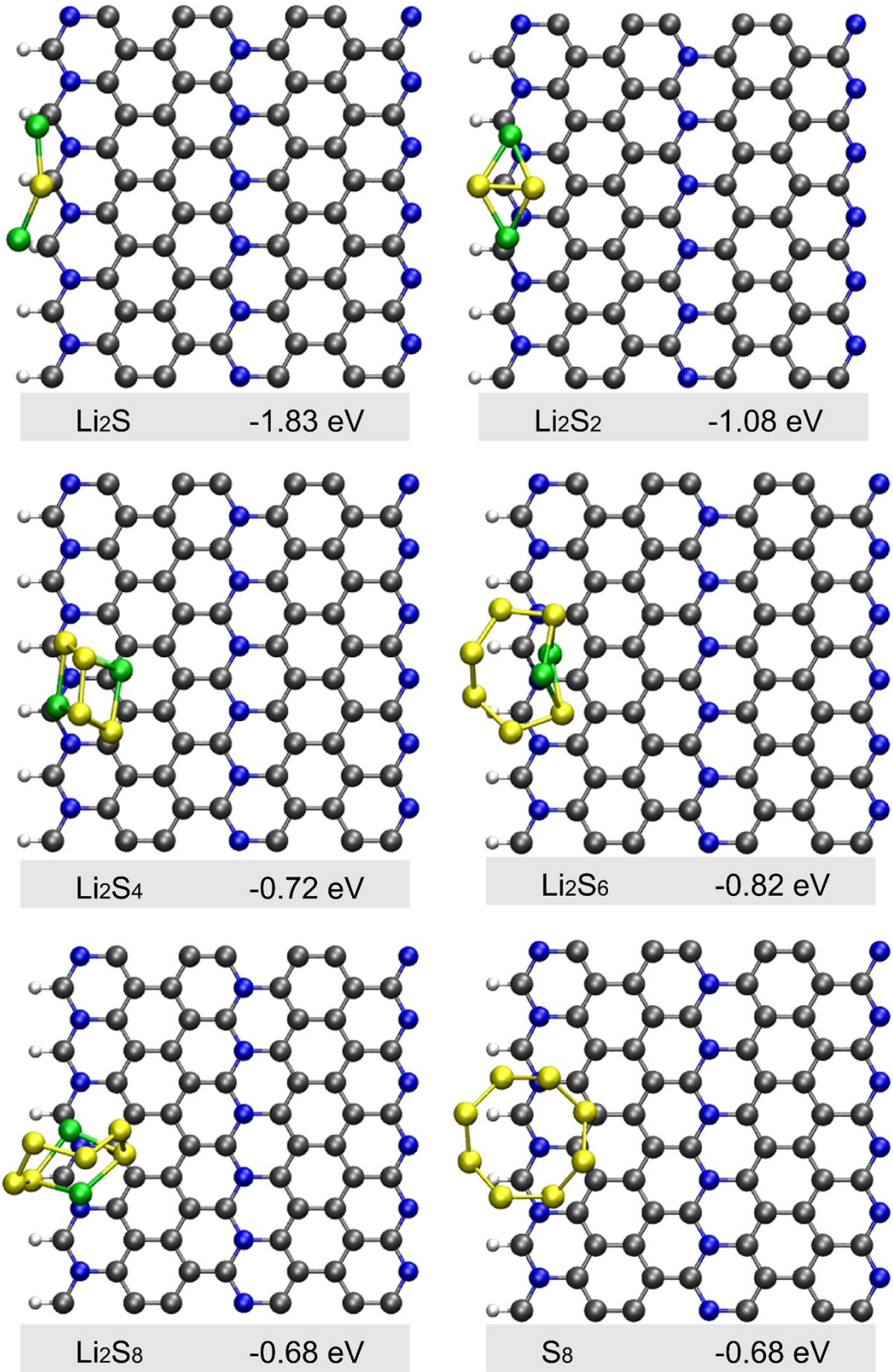

Fig. S10. Optimized structures of LiPs adsorbed on the O-Z-**C2N0**-C0N2 nanoribbon, and corresponding E_{ads}.

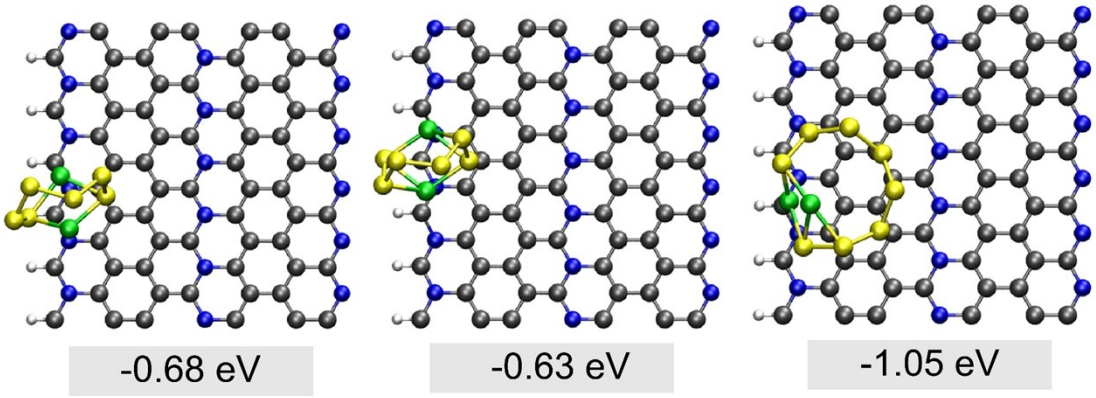

Fig. S11. Optimized structures of Li_2S_6 adsorbed on the O-Z-**C2N0**-C0N2 nanoribbon, and corresponding E_{ads}.

Reference

[1] Q. He, B. Yu, H. Wang, M. Rana, X. Liao, and Y. Zhao, Oxygen defects boost polysulfides immobilization and catalytic conversion: First-principles computational characterization and experimental design, Nano Res. 13 (2020) 2299-2307.

[2] D. Wang, H. Li, L. Zhang, Z. Sun, D. Han, L. Niu, and J. Zhao, 2D Nitrogen-Containing Carbon Material C_5N as Potential Host Material for Lithium Polysulfides: A First-Principles Study, Adv. Theory Simul. 2 (2018) 1800165-1800172.