Energy Materials

Supplementary Materials

Beyond point defects: a first-principles investigation of topological line defects in graphene as continuous catalytic highways for Li-S batteries

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Calculation Details

The Reduction of S_8 to Li_2S Process

The equations for the reduction of S_8 to Li_2S process (the sulfur reduction reaction) can be presented as follows[1,2]:

$$S_8^* + 16Li^+ + 2e^- \rightarrow Li_2S_8^* + 14Li^+$$

$$Li_2S_8^* + 14Li^+ + 2e^- \rightarrow Li_2S_6^* + Li_2S_2 + 12Li^+$$

$$Li_2S_6^* + Li_2S_2 + 12Li^+ + 2e^- \rightarrow Li_2S_4^* + 2Li_2S_2 + 10Li^+$$

$$Li_2S_4^* + 2Li_2S_2 + 10Li^+ + 2e^- \rightarrow Li_2S_2^* + 3Li_2S_2 + 8Li^+$$

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

where the star "*" refers to the active site on the catalytic surface.

The Charge Density Difference $\Delta\rho$ after Li_2S Adsorption

The $\Delta\rho$ is calculated using the following equation[3]:

$$\Delta\rho = \rho_{total} - \rho_{PS} - \rho_{LD}$$

where ρ_{total}, ρ_{PS}, and ρ_{LD} respectively represent the charge density after the adsorption of polysulfide, the charge density of polysulfide clusters, and the charge density of the substrate before adsorption.

Table S1. The adsorption energies of S_8 and LiPSs in the pristine graphene and the line-defect graphene

	Li_2S	Li_2S_2	Li_2S_4	Li_2S_6	Li_2S_8	S_8
Graphene	-0.88	-0.72	-0.59	-0.66	-0.45	-0.55
d5d7G	-1.72	-1.31	-0.87	-0.74	-1.17	-0.84
t5t7G	-1.74	-1.68	-1.16	-1.06	-1.21	-0.89
585G	-1.86	-1.69	-1.21	-1.10	-1.25	-0.90

Table S2. The variations in the Li-S bond length (Δd_{Li-S}) and the bond angle ($\Delta\alpha$), the charge transfer (ΔQ) and the adsorption energy (E_a) after Li_2S adsorption

	Δd_{Li-S} (Å)	$\Delta\alpha$ (°)	ΔQ (e)	E_{ad} (eV)
Graphene	0.01	1.60	-0.31	-0.88
d5d7G	0.16	4.50	-0.65	-1.72
t5t7G	0.21	5.30	-0.78	-1.74
585G	0.24	13.80	-0.99	-1.86

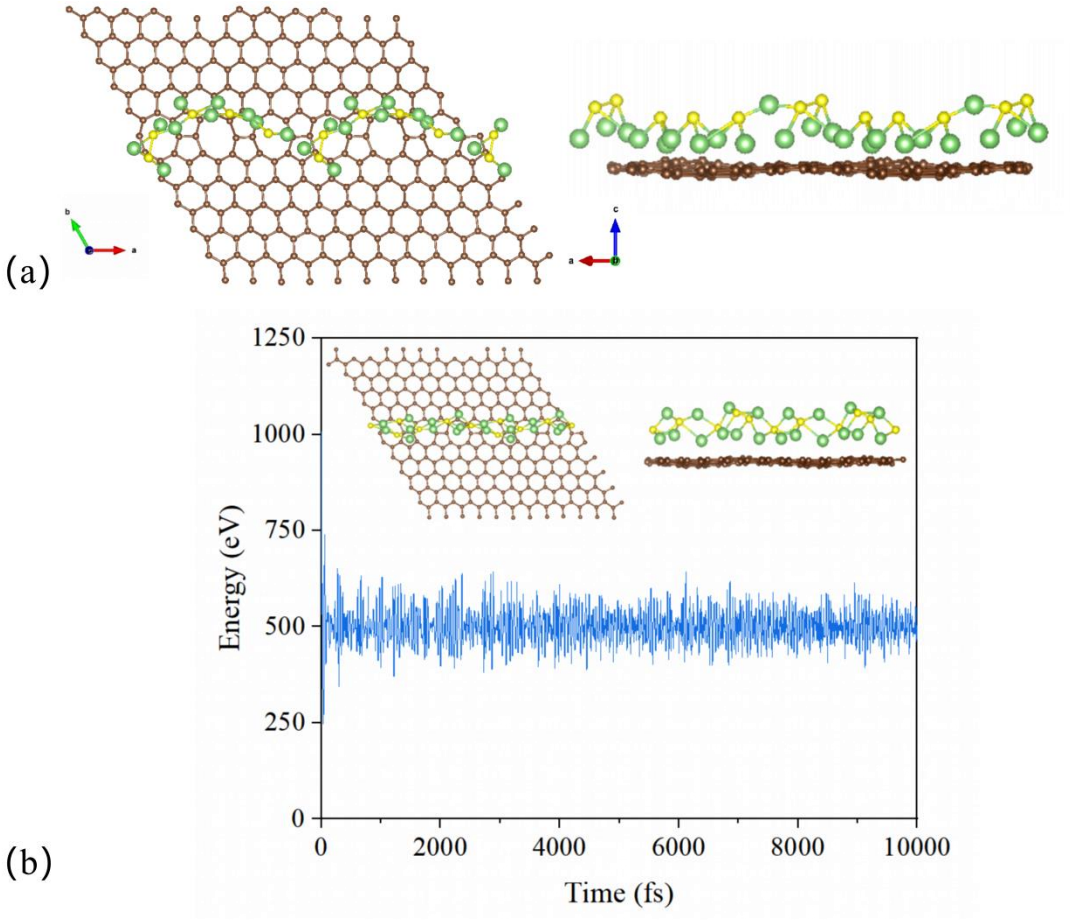

Fig.S1. (a) The top and side views of the initial model of the $(Li_2S)_n$ cluster placed away from the 585G line defect. (b) Total energy evolution profile of the system during the AIMD simulation at 500 K for 10,000 fs, along with the corresponding top and side views of the final simulation snapshot.

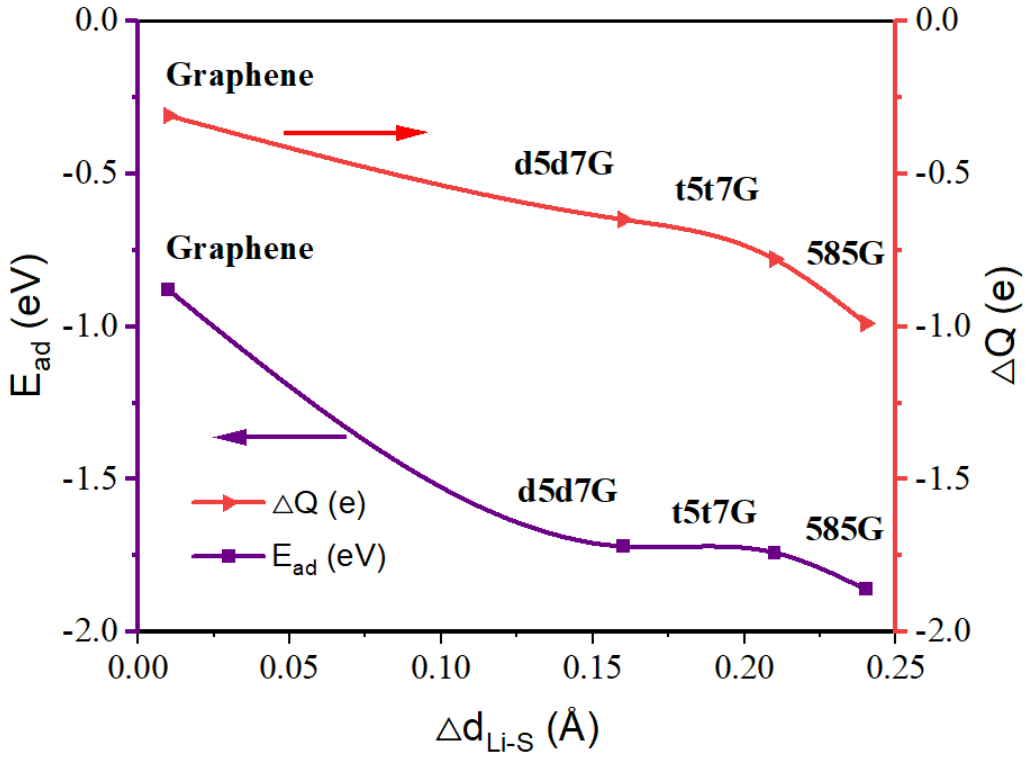

Fig. S2. Changes in the average Li-S bond length correlate with the adsorption energy and the amount of charge transfer upon Li_2S adsorption.

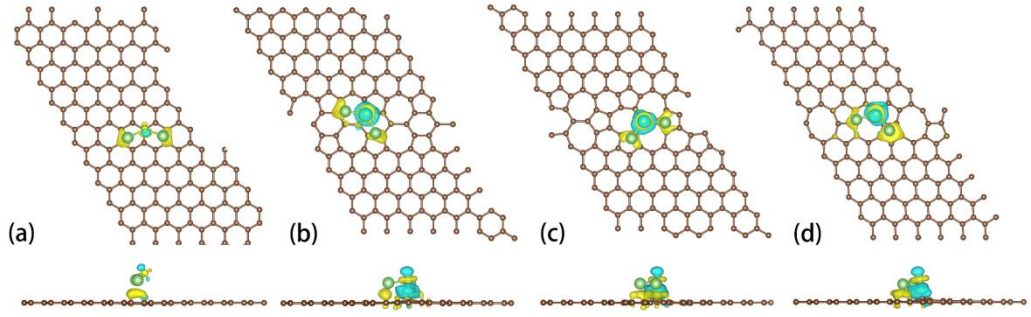

Fig. S3. Charge density difference of Li_2S molecule absorbed on (a) graphene, (b) d5d7G, (c) t5t7G and (d) 585G. The isosurface is set to 0.005 e/Bohr^3.

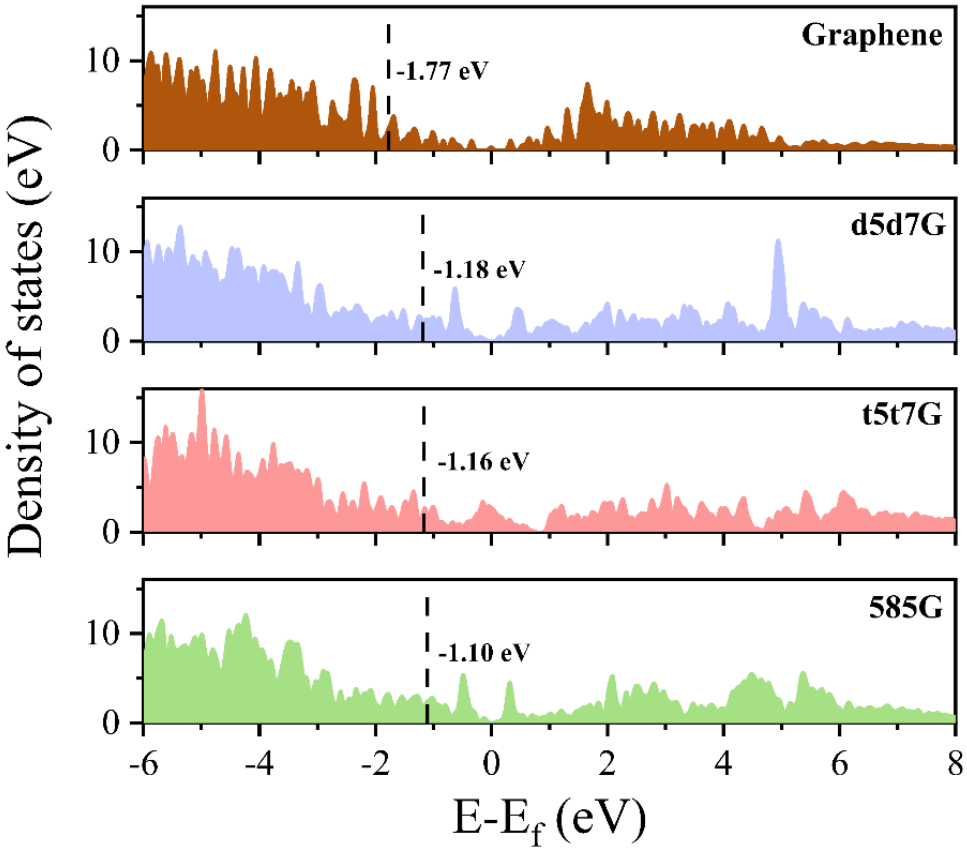

Fig. S4. Density of states analysis of the *p* bands of graphene, d5d7G, t5t7G, and 585G.

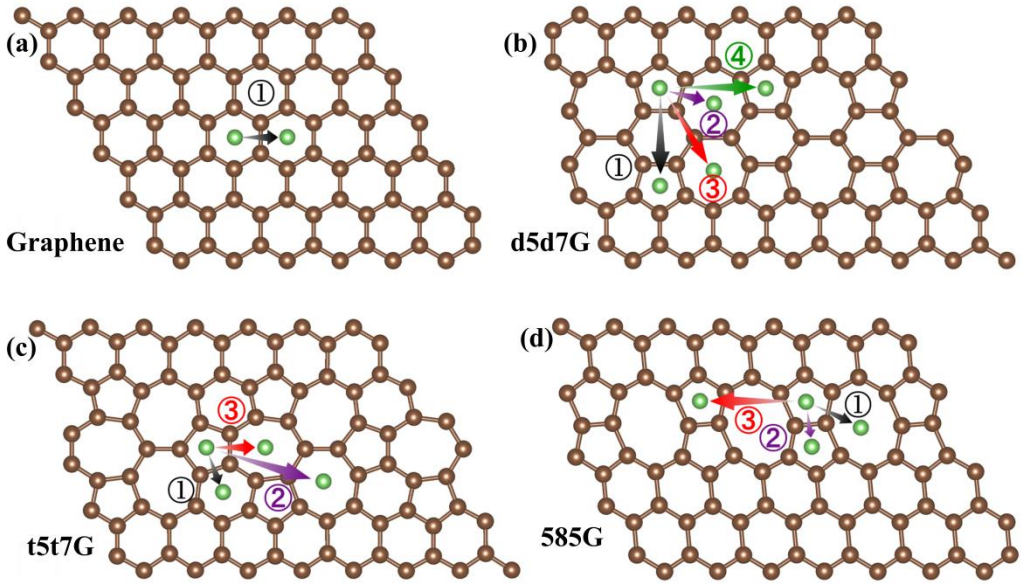

Fig. S5. The diffusion paths of Li^+ transport in (a) graphene, (b) d5d7G, (c) t5t7G, and (d) 585G.

REFERENCES

[1] He, Q.; Yu, B.; Wang, H.; Rana, M.; Liao, X.; Zhao, Y. Oxygen defects boost polysulfides immobilization and catalytic conversion: First-principles computational characterization and experimental design. *Nano Res.* **2020**, *13*, 2299-2307, doi:10.1007/s12274-020-2850-5.

[2] Yu, B.; He, Q.; Zhao, Y. Exploring the anchoring effect and catalytic mechanism of 3d transition metal phthalocyanine for S8/LiPSs: A density functional theory study. *Appl. Surf. Sci.* **2021**, *558*, 149928, doi:10.1016/j.apsusc.2021.149928.

[3] Zhao, Y.; Xi, Y.; Zhu, Y.; et al. The synergistic effect of heteronuclear diatom enhances the catalytic and adsorption ability of lithium-sulfur batteries. *Appl. Surf. Sci.* **2025**, *706*, 163600, doi:10.1016/j.apsusc.2025.163600.