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Supporting Information

Single atom catalysts supported on N-doped graphene toward fast kinetics in Li–S batteries: a theoretical study

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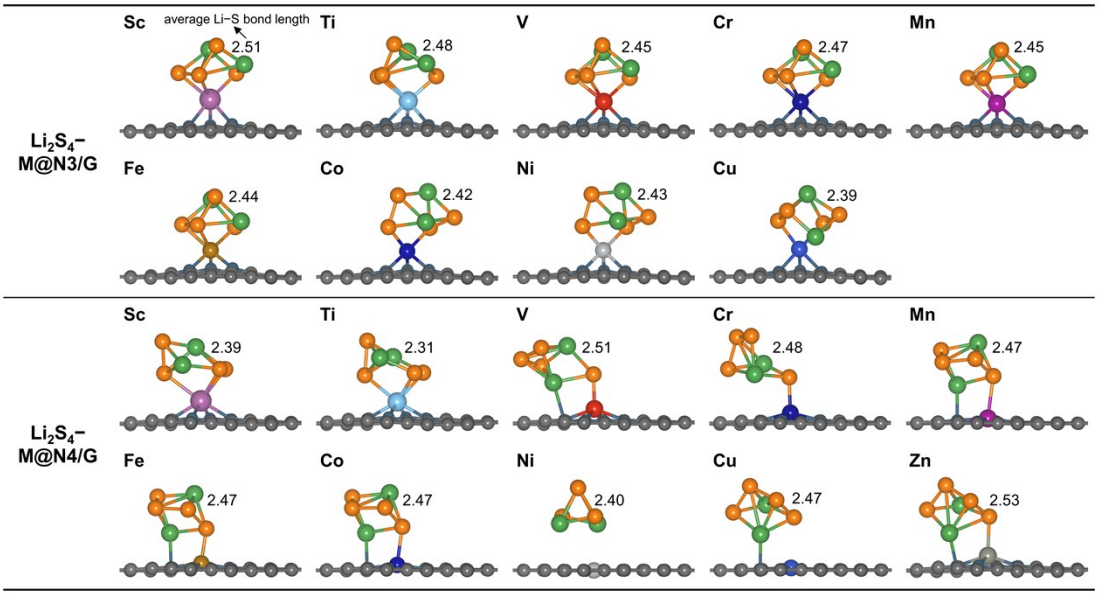

Fig. S1 Optimized adsorption structures of Li_2S_4 on M_{3d}@N/G. C, gray; N, blue; Li, green; and S, orange. The numbers given for each structure are average bond lengths of Li−S bonds in Å. Note that there is not a clear relationship between the average lengths of Li−S bonds in the adsorbed Li_2S_4 and that of the isolated Li_2S_4 molecule (2.51 Å), because not only the lengths of Li−S bonds but also the lengths of S−S bonds would change once the Li_2S_4 is adsorbed.

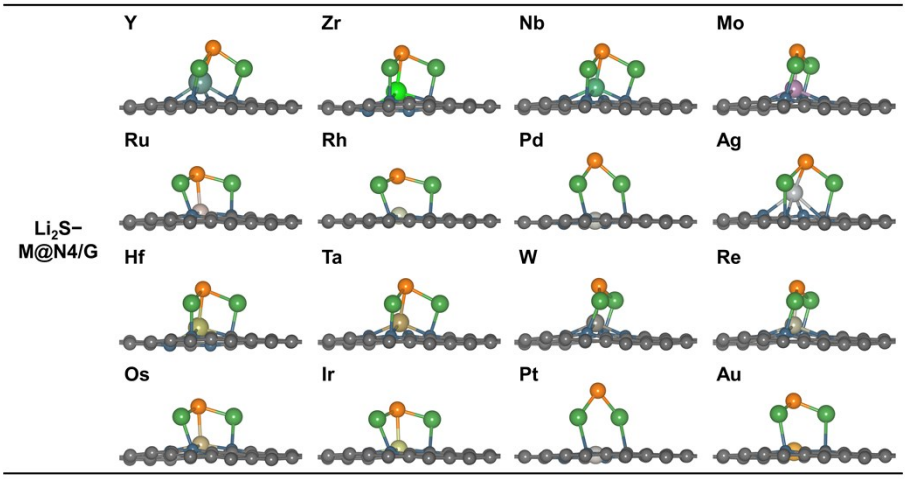

Fig. S2 Optimized adsorption structures of Li_2S on $M_{4d,5d}$@N4/G. C, gray; N, blue; Li, green; and S, orange.

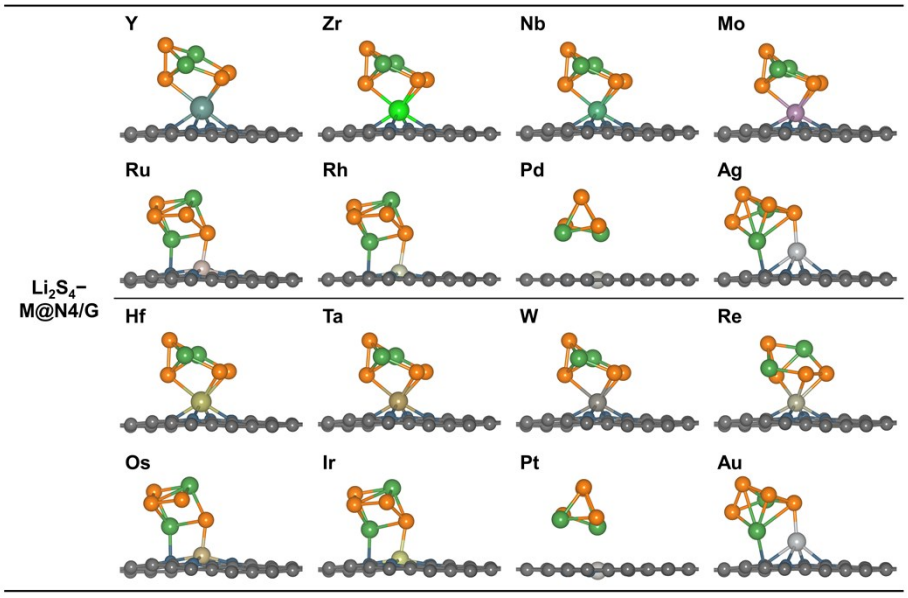

Fig. S3 Optimized adsorption structures of Li_2S_4 on $M_{4d,5d}$@N4/G. C, gray; N, blue; Li, green; and S, orange.

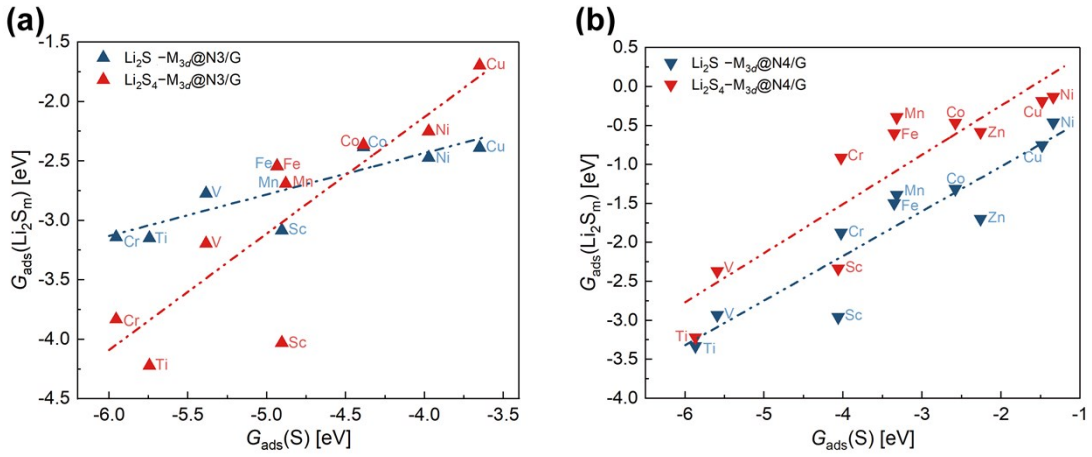

Fig. S4 The relationships about $G_{ads}(Li_2S)$ and $G_{ads}(Li_2S_4)$ versus $G_{ads}(S)$ on (a) M_{3d}@N3/G and (b) M_{3d}@N4/G.

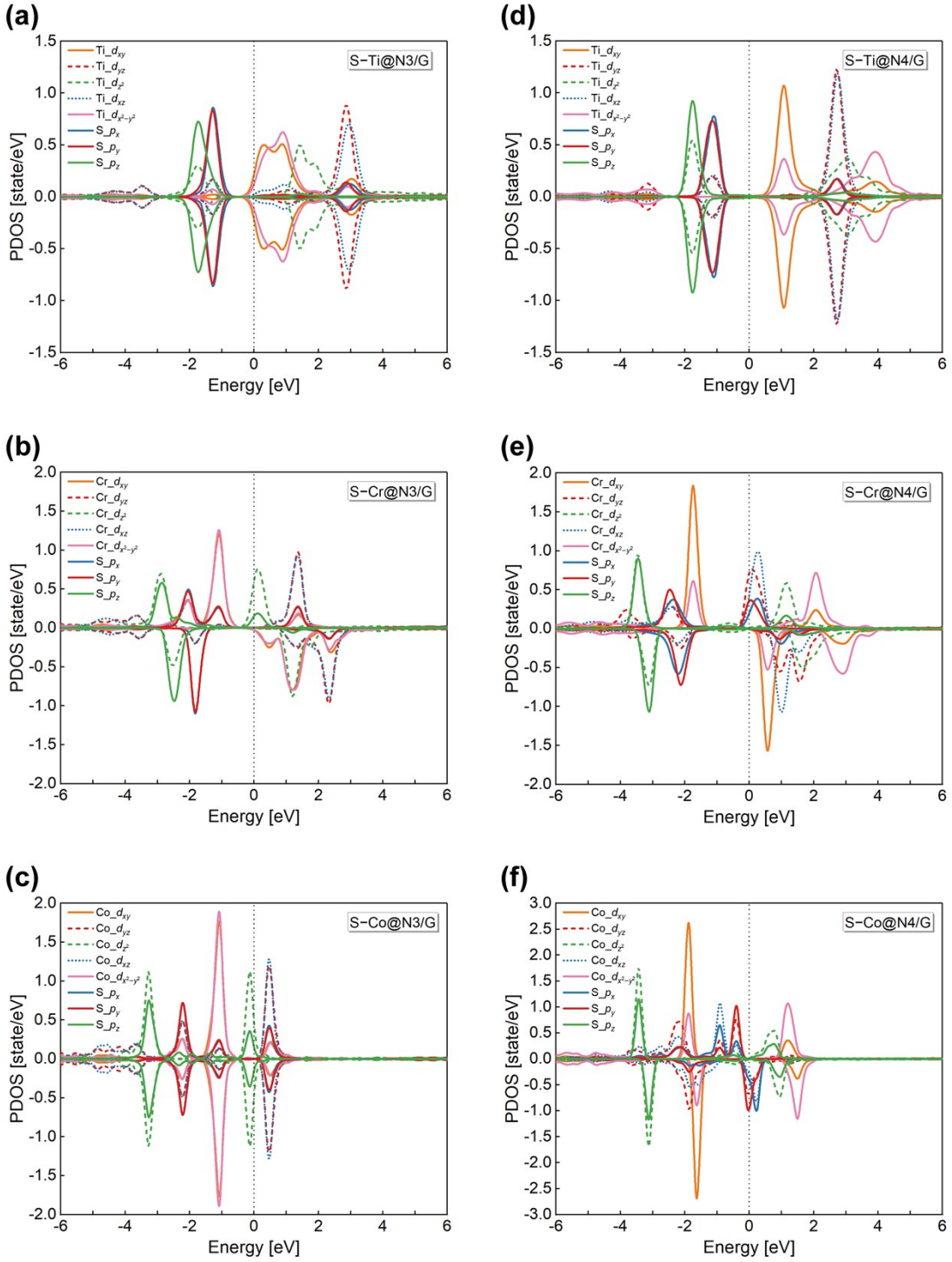

Fig. S5 PDOS profiles of S-atom adsorption on (a) Ti@N3/G, (b) Cr@N3/G, (c) Co@N3/G, (d) Ti@N4/G, (e) Cr@N4/G, and (f) Co@N4/G. The Fermi energy level is set to zero and indicated by the gray dotted line.

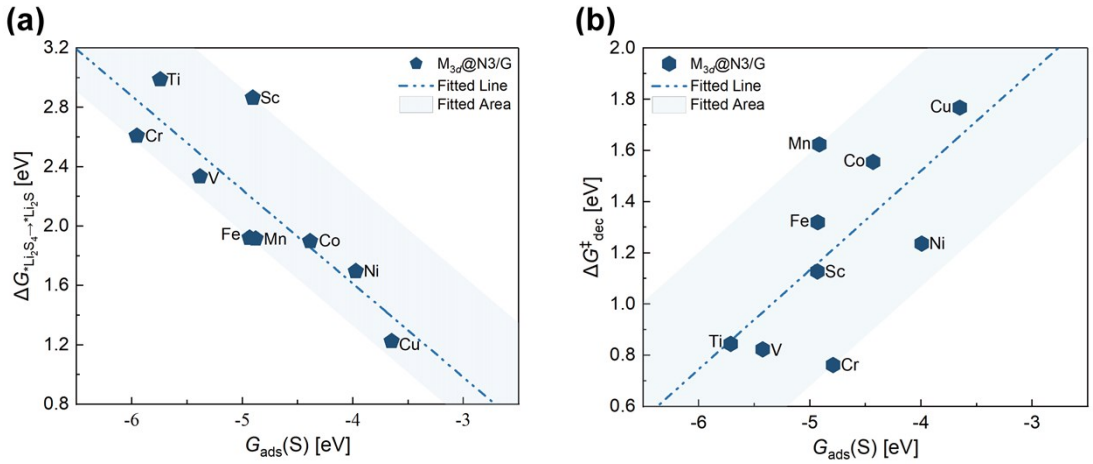

Fig. S6 G_{ads}(S) versus (a) $\Delta G_{*Li_2S_4 \rightarrow *Li_2S}$ and (b) $\Delta G^{\ddagger}_{dec}$ on M_{3d}@N3/G. The symbols are the calculated data. The fitted area is built based on the maximum deviation of data from the fitted line.

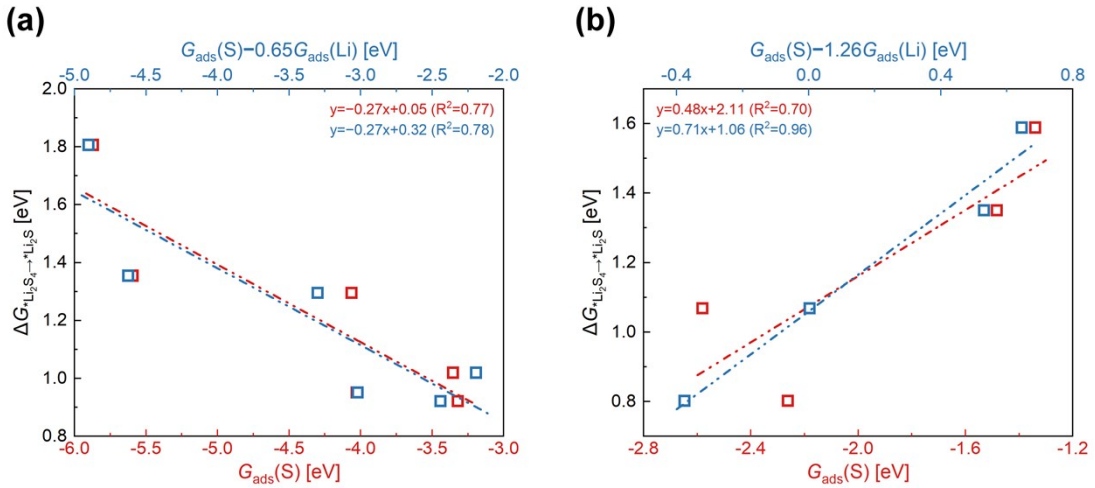

Fig. S7 Comparsion of the single descriptor, G_{ads}(S) (in red), and the double descriptor, G_{ads}(S) + γG_{ads}(Li) (in blue), versus the $\Delta G_{*Li_2S_4 \rightarrow *Li_2S}$ on M_{3d}@N4/G, where (a) is for early M_{3d} (Sc to Fe) and (b) is for late M_{3d} (Co to Zn).

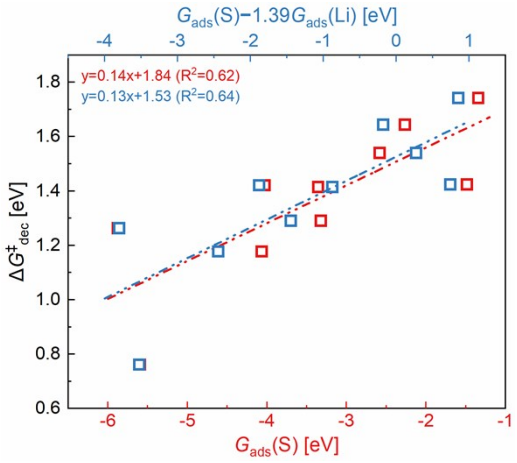

Fig. S8 Comparsion of the relationships about the $\Delta G^{\ddagger}_{dec}$ on M_{3d}@N4/G versus single descriptor (in red): G_{ads}(S), and double descriptor (in blue): G_{ads}(S) + γG_{ads}(Li).

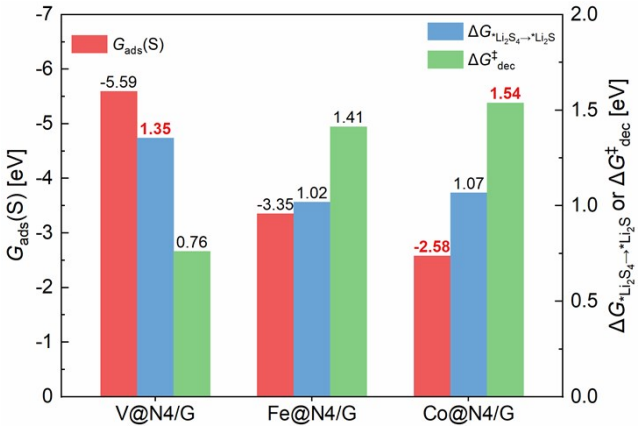

Fig. S9 Our calculated G_{ads}(S), ΔG*$Li_2S_4 \rightarrow$*Li_2S, $\Delta G^{\ddagger}_{dec}$ on the three ever-reported catalysts: V@N4/G, Fe@N4/G, and Co@N4/G.

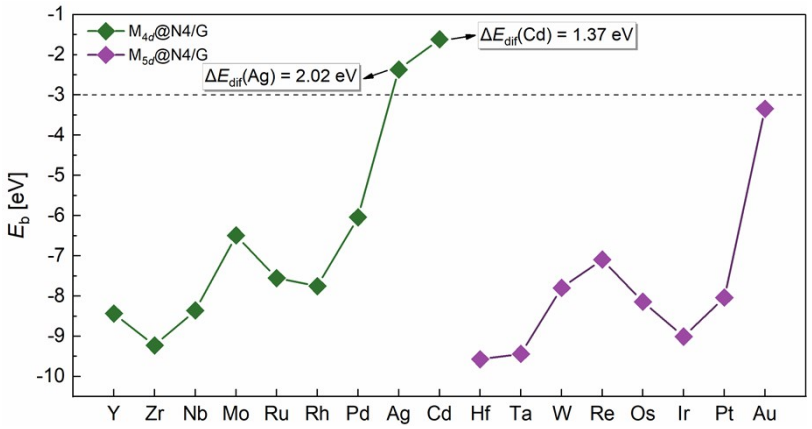

Fig. S10 Binding energies (E_b) of $M_{4d,5d}$@N4/G. The values of diffusion energy difference (ΔE_{dif}) of Ag@N4/G and Cd@N4/G are labeled. The dash line stands for the filter value of −3 eV.

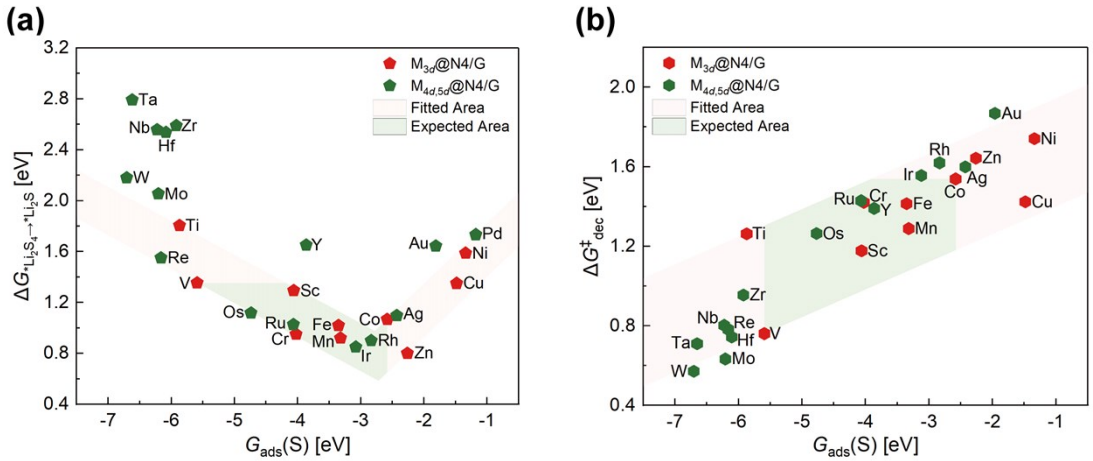

Fig. S11 Relationships between G_{ads}(S) and (a) $\Delta G_{*Li_2S_4 \rightarrow *Li_2S}$ and (b) $\Delta G^{\ddagger}_{dec}$ on M@N4/G. The values of Pt@N4/G are not marked because of its positive G_{ads}(S), and $\Delta G^{\ddagger}_{dec}$ of Pd@N4/G is also not given because the stable decomposed structures of Li_2S on it cannot be found.

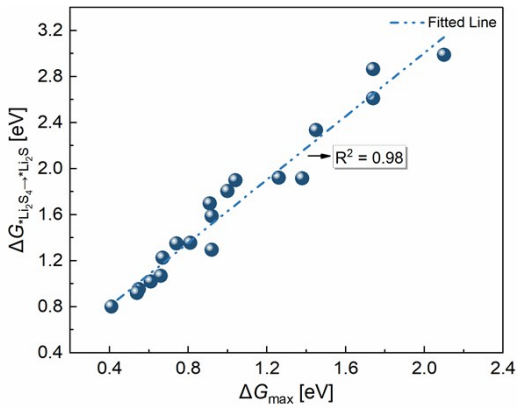

Fig. S12 $\Delta G_{*Li_2S_4 \rightarrow *Li_2S}$ versus ΔG_{max} on M_{3d}@N/G. ΔG_{max} is the maximum of the free energy changes of steps R1 and R2.

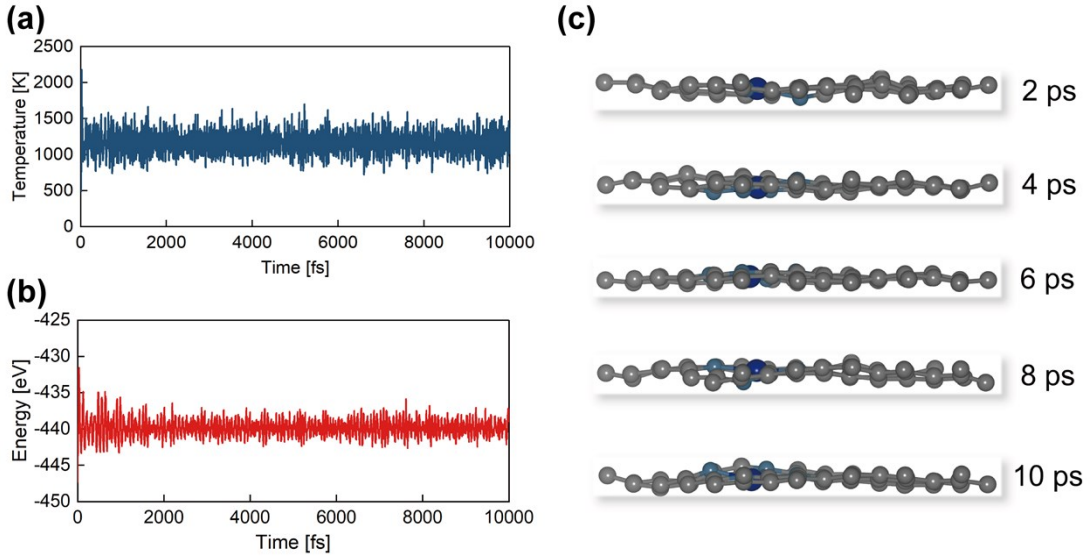

Fig. S13 Variations of (a) temperature and (b) energy over a total time period of 10 ps for the AIMD simulation of Cr@N4/G at 900 ℃. (c) Five snapshots of simulated structures of Cr@N4/G at 2 ps, 4 ps, 6 ps, 8 ps, and 10 ps, respectively.

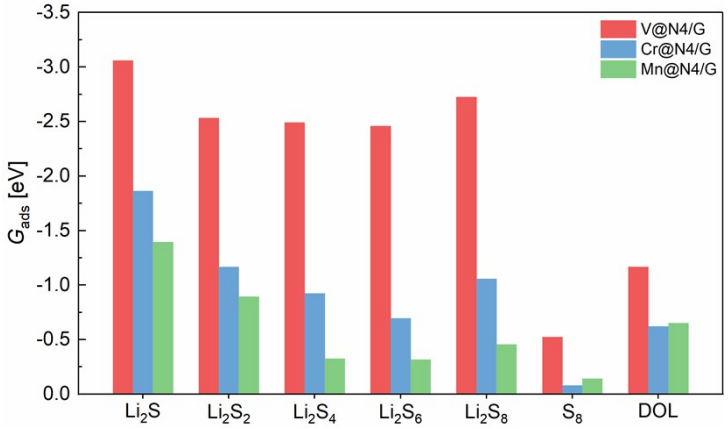

Fig. S14 Comparison of adsorption free energies (G_{ads}) of sulfur species and DOL solvent molecule on V@N4/G, Cr@N4/G, and Mn@N4/G.

The stability of Cr@N4/G and Mn@N4/G during charge−discharge process

Apart from the feasibility of experimental synthesis, the stability of single atoms (Cr and Mn) during charge−discharge process was also important and should be considered. However, because of expensive computational cost, it is hard to fully (or directly) describe the complex charge−discharge process including the various sulfur species and electrolyte environment. Here we make a reasonable simplification by comparing the interactions of various sulfur species and solvent molecules (we take 1,3-dioxolane (DOL) as an example) with the V, Cr, and Mn@N4/G. The calculated adsorption energies shown in Fig. S14 indicate that sulfur species and DOL all interact more tensely with V@N4/G than with Cr@N4/G and Mn@N4/G. Since V@N4/G has been demonstrated experimentally enough stability working in the system of Li−S batteries,[1,2] we can indirectly conclude that Cr and Mn single atoms can also keep stable on their corresponding M@N4/G framework during charge−discharge process.

[1] Y. Fan, F. Ma, J. Liang, X. Chen, Z. Miao, S. Duan, L. Wang, T. Wang, J. Han, R. Cao, S. Jiao and Q. Li, *Nanoscale*, 2020, **12**, 584−590.
[2] G. Zhou, S. Zhao, T. Wang, S. Z. Yang, B. Johannessen, H. Chen, C. Liu, Y. Ye, Y. Wu, Y. Peng, C. Liu, S. P. Jiang, Q. Zhang and Y. Cui, *Nano Lett.*, 2020, **20**, 1252−1261.

Table S1 Tests of various valence states of transition metals for Mn-containing systems.[a]

System	M_{test} (μ_B)	M_{opt} (μ_B)	E_{opt} (eV)	M_{select} (μ_B)
Mn@N3/G	0	0	-459.13	5
	1	0	-459.17	
	2	0	-459.17	
	3	5	-459.65	
	4	5	-459.65	
	5	5	-459.65	
Li_2S−Mn@N3/G	0	2	-470.49	5
	1	0	-470.23	
	2	0	-470.23	
	3	5	-471.00	
	4	5	-471.00	
	5	5	-471.00	
Li_2S_4−Mn@N3/G	0	1	-485.34	3
	1	3	-485.88	
	2	3	-485.88	
	3	3	-485.88	
	4	3	-485.88	
	5	3	-485.88	
Mn@N4/G	0	3	-451.71	3
	1	0	-450.40	
	2	3	-451.71	
	3	3	-451.71	
	4	3	-451.71	
	5	3	-451.71	
Li_2S−Mn@N4/G	0	0	-461.46	2
	1	2	-461.83	
	2	2	-461.83	
	3	2	-461.83	
	4	2	-461.83	
	5	2	-461.83	
Li_2S_4−Mn@N4/G	0	0	-475.10	3
	1	0	-475.10	
	2	3	-475.53	
	3	3	-475.53	
	4	3	-475.53	
	5	3	-475.53	

[a]In this table, M_{test} and M_{opt} are the magnetic moments of input structures and optimized structures, respectively. E_{opt} denote the energies of optimized structures and M_{select} denote the final-determined magnetic moments for further investigations.

Table S2 Calculated $G_{ads}(Li_2S)$, $G_{ads}(Li_2S_4)$, $G_{ads}(S)$, $\Delta G_{*Li_2S_4 \rightarrow *Li_2S}$, and $\Delta G^{\ddagger}_{dec}$ (in eV) on M@N/G.

Support	M	$G_{ads}(Li_2S)$	$G_{ads}(Li_2S_4)$	$G_{ads}(S)$	$\Delta G_{*Li_2S_4 \rightarrow *Li_2S}$	$\Delta G^{\ddagger}_{dec}$
M@N3/G	Sc	-3.08	-4.03	-4.90	2.86	1.13
	Ti	-3.15	-4.22	-5.74	2.99	0.84
	V	-2.77	-3.19	-5.38	2.33	0.82
	Cr	-3.14	-3.83	-5.95	2.61	0.76
	Mn	-2.69	-2.69	-4.88	1.92	1.62
	Fe	-2.54	-2.55	-4.93	1.92	1.32
	Co	-2.38	-2.36	-4.39	1.90	1.56
	Ni	-2.47	-2.25	-3.97	1.70	1.24
	Cu	-2.39	-1.70	-3.65	1.22	1.77
M@N4/G	Sc	-2.96	-2.34	-4.06	1.29	1.18
	Ti	-3.33	-3.22	-5.87	1.81	1.26
	V	-2.93	-2.37	-5.59	1.35	0.76
	Cr	-1.88	-0.91	-4.03	0.95	1.42
	Mn	-1.39	-0.39	-3.32	0.92	1.29
	Fe	-1.50	-0.60	-3.35	1.02	1.41
	Co	-1.31	-0.47	-2.58	1.07	1.54
	Ni	-0.46	-0.13	-1.34	1.59	1.74
	Cu	-0.75	-0.19	-1.48	1.35	1.42
	Zn	-1.70	-0.58	-2.26	0.80	1.64
	Y	-2.75	-2.48	-3.86	1.65	1.39
	Zr	-3.49	-4.16	-5.92	2.59	0.95
	Nb	-3.37	-4.01	-6.23	2.56	0.80
	Mo	-3.12	-3.26	-6.21	2.05	0.63
	Ru	-2.41	-1.52	-4.07	1.03	1.43
	Rh	-1.50	-0.48	-2.83	0.90	1.62
	Pd	-0.35	-0.17	-1.18	1.73	N/A

	Ag	-1.93	-1.11	-2.43	1.10	1.60
	Hf	-3.63	-4.25	-6.11	2.54	0.74
	Ta	-3.51	-4.38	-6.65	2.79	0.71
	W	-3.36	-3.63	-6.70	2.18	0.57
M@N4/G	Re	-3.12	-2.75	-6.16	1.55	0.78
	Os	-2.50	-1.70	-4.77	1.12	1.26
	Ir	-1.53	-0.46	-3.12	0.85	1.56
	Pt	0.27	0.37	0.10	N/A	N/A
	Au	-0.29	-0.02	-1.96	1.64	1.87

Table S3 Calculated −IpCOHP of different atom pairs between adsorbed Li_2S or Li_2S_4 and M_{3d}@N/G.

Support	Adsorbate	M	Atom pair					
			S−M	Li−N	Li−C	S−N	S−C	Li−M
M@N3/G	Li_2S	Sc	2.29	0.45	0.43	0	0	0
		Ti	2.50	1.03	0.56	0	0	0.02
		V	2.24	1.15	0.50	0	0	-0.03
		Cr	2.89	0.59	0.40	0	0	0.24
		Mn	2.37	0.58	0.39	0	0	0.28
		Fe	2.49	0.50	0.39	0	0	0.22
		Co	2.42	0.81	0.31	0	0	0.30
		Ni	2.36	0.69	0.32	0	0	0.34
		Cu	1.96	0.66	0.30	0	0	0.31
M@N3/G	Li_2S_4	Sc	1.88	0	0	0	0	0
		Ti	1.83	0	0	0	0	0
		V	1.51	0	0	0	0	0
		Cr	2.12	0	0	0	0	0
		Mn	2.02	0	0	0	0	0.30
		Fe	1.94	0.35	0	0.09	0	0.29
		Co	2.80	0	0	0.16	0	0.30
		Ni	2.48	0	0	0.21	0	0.29
		Cu	1.80	0.42	0.37	0	0	0.30
M@N4/G	Li_2S	Sc	2.54	1.03	0.42	0	0	0.01
		Ti	2.82	1.32	0.53	0	0	0.01
		V	2.65	1.41	0.49	0	0	-0.05
		Cr	2.71	0.95	0.31	0	0	0.23
		Mn	2.34	1.00	0.33	0	0	0.22
		Fe	1.99	0.96	0.33	0	0	0.23
		Co	1.38	0.91	0.34	0	0	0.21
		Ni	0.27	0.89	0.29	0	0	0.21

		Cu	1.16	0.88	0.35	0	0	0.23
		Zn	1.46	0.91	0.30	0	0	0.35
M@N4/G	Li_2S_4	Sc	1.48	0	0	0.15	0	0
		Ti	1.61	0	0	0.32	0	0
		V	3.23	1.10	0.54	0	0	0.28
		Cr	2.50	0.90	0.27	0	0	0.21
		Mn	0.91	0.90	0.26	0	0	0.21
		Fe	2.65	0.94	0.30	0.17	0	0.24
		Co	1.29	0.89	0.26	0	0	0.21
		Ni	0	0	0.21	0	0	0.33
		Cu	0	0.69	0.31	0	0	0.19
		Zn	1.17	0.67	0.38	0	0	0.34

Table S4 Calculated free energy changes (in eV) for step R1 (ΔG_1) and step R2 (ΔG_2).[a]

Support	M3	ΔG_1	ΔG_2
M@N3/G	Sc	**1.74** [b]	1.13
	Ti	**2.10**	0.89
	V	**1.45**	0.89
	Cr	**1.74**	0.86
	Mn	**1.38**	0.53
	Fe	**1.26**	0.66
	Co	0.86	**1.04**
	Ni	**0.91**	0.79
	Cu	0.55	**0.67**
M@N4/G	Sc	0.37	**0.92**
	Ti	**1.00**	0.80
	V	0.55	**0.81**
	Cr	0.40	**0.55**
	Mn	**0.54**	0.38
	Fe	**0.61**	0.41
	Co	**0.66**	0.41
	Ni	**0.92**	0.67
	Cu	**0.74**	0.61
	Zn	**0.41**	0.39

[a] R1: $*Li_2S_2 \rightarrow *Li_2S + (1/8)\ S_8$; R2: $*Li_2S_4 \rightarrow *Li_2S_2 + (1/4)S_8$.

[b] The maximum (ΔG_{max}) of ΔG_1 and ΔG_2 is bold, corresponding to the rate-determining step.