Electronic Supplementary Material (ESI) for Nanoscale.
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Doping Strategy to Regulate the Adsorption Energy of Li_2S_4 and Li_2S to Promote Sulfur Reduction on Chevrel Phase Mo_6Se_8 in Lithium–Sulfur Battery

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1.1 Adsorption of LiPSs

(a)

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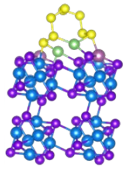
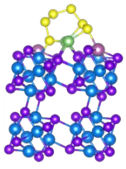
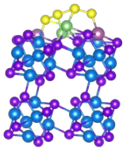
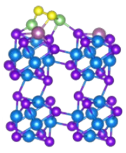
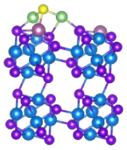
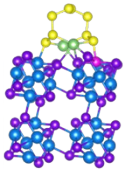
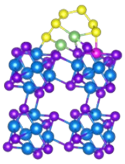
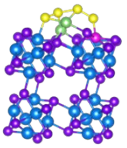
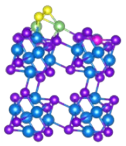
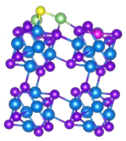
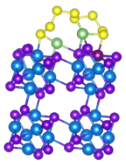
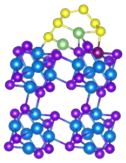
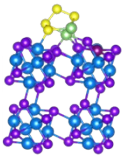
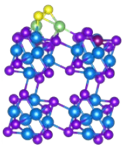
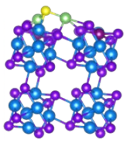
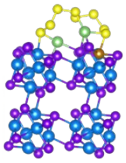
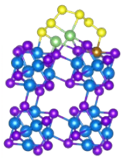
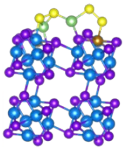
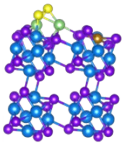
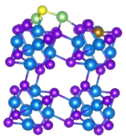
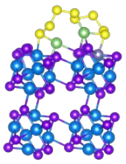
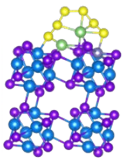
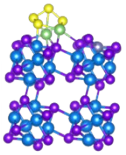
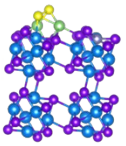
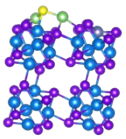
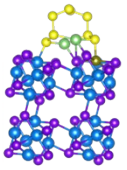
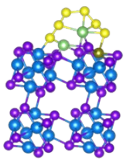
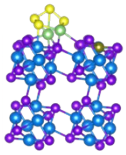
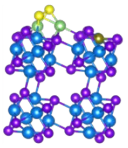
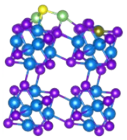
Sc@Mo_6Se_8	 -3.47 eV	 -3.07 eV	 -3.08 eV	 -3.60 eV	 -4.11 eV
Cr@Mo_6Se_8	 -2.97 eV	 -2.78 eV	 -2.74 eV	 -3.45 eV	 -4.09 eV
Mn@Mo_6Se_8	 -3.33 eV	 -2.79 eV	 -2.63 eV	 -3.44 eV	 -4.02 eV
Fe@Mo_6Se_8	 -3.27 eV	 -3.05 eV	 -2.82 eV	 -3.34 eV	 -3.91 eV
Co@Mo_6Se_8	 -3.23 eV	 -2.72 eV	 -3.01 eV	 -3.44 eV	 -3.97 eV
Ni@Mo_6Se_8	 -2.55 eV	 -2.40 eV	 -2.81 eV	 -3.23 eV	 -3.76 eV
	Mo	Se	Li	S	

(b)

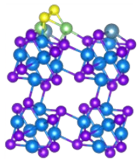
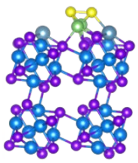
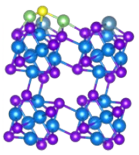
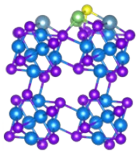
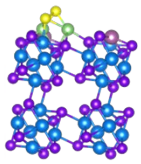
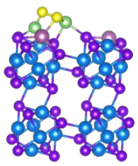
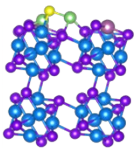
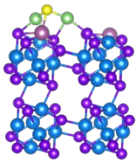
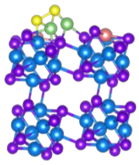
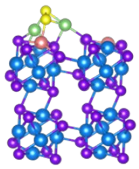
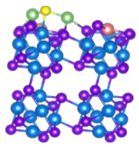
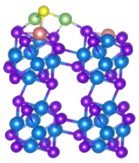
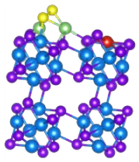
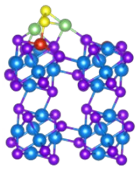
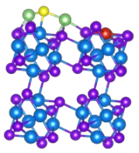
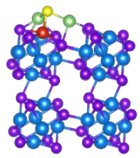
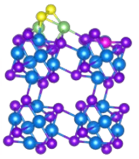
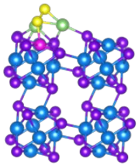
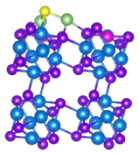
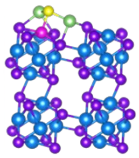
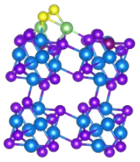
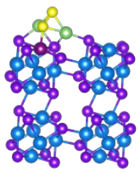
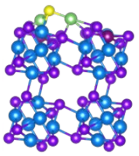
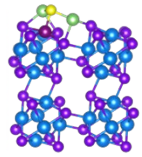
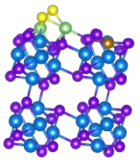
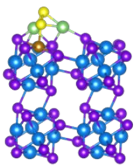
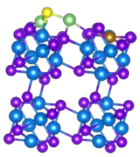
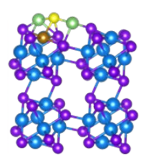
	Li_2S_2* Mo site	Li_2S_2* M site	Li_2S* Mo site	Li_2S* M site
$Ca@Mo_6Se_8$	 -3.33 eV	 -2.73 eV	 -3.98 eV	 -3.60 eV
$Sc@Mo_6Se_8$	 -3.21 eV	 -3.67 eV	 -3.74 eV	 -4.11 eV
$Ti@Mo_6Se_8$	 -3.30 eV	 -3.57 eV	 -3.94 eV	 -4.43 eV
$V@Mo_6Se_8$	 -3.38 eV	 -3.46 eV	 -4.09 eV	 -4.23 eV
$Cr@Mo_6Se_8$	 -3.45 eV	 -3.23 eV	 -4.09 eV	 -3.91 eV
$Mn@Mo_6Se_8$	 -3.43 eV	 -3.01 eV	 -4.09 eV	 -3.67 eV
$Fe@Mo_6Se_8$	 -3.34 eV	 -3.05 eV	 -3.97 eV	 -3.65 eV

Figure S1. (a) Adsorption energies and adsorption configurations of LiPSs on $M@Mo_6Se_8$ systems (b) Adsorption energies and adsorption configurations of Li_2S_n (n = 2 and 1) at different active sites on $M@Mo_6Se_8$ systems.

1.2 Charge density difference

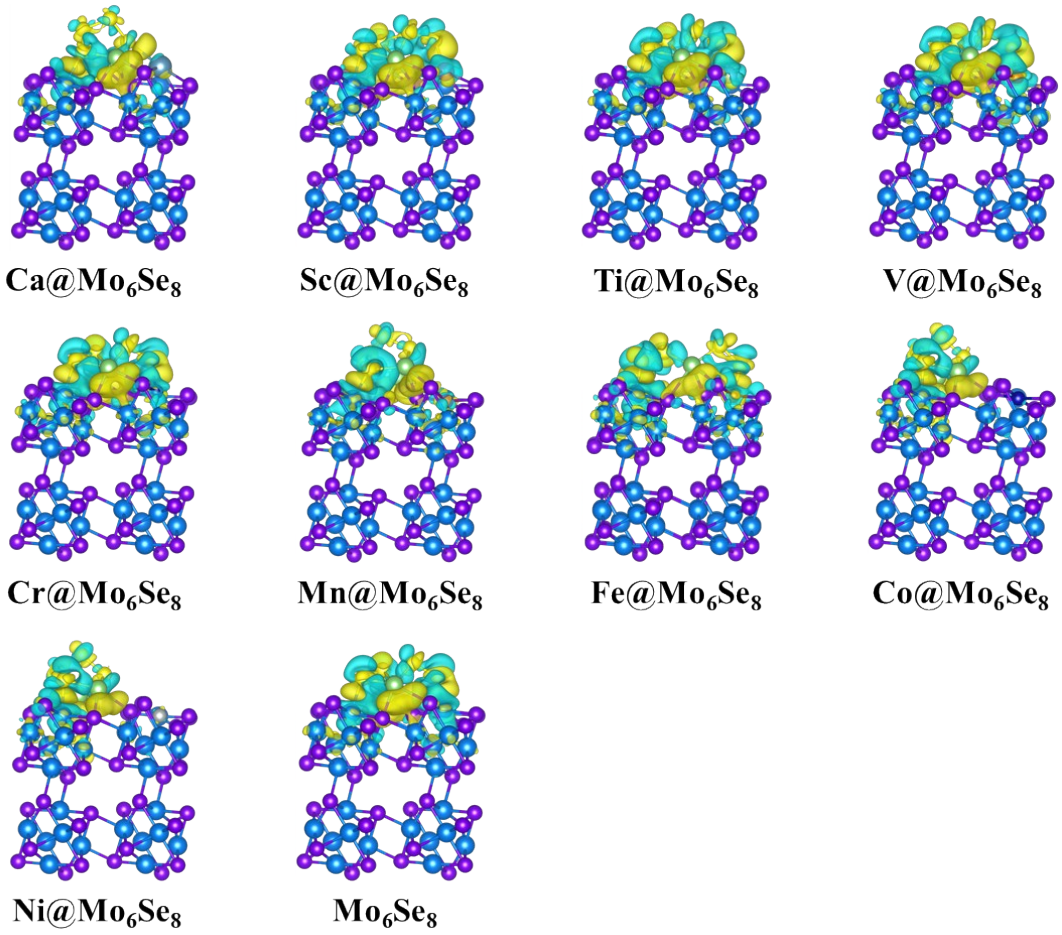


Figure S2. The charge density difference between the Li_2S_4 and various catalyst surfaces. The yellow and cyan represent the gain and loss regions of the electrons, respectively. The equivalence plane is set to 0.002 eV/Å^3.

1.3 Projected density of states (PDOS)

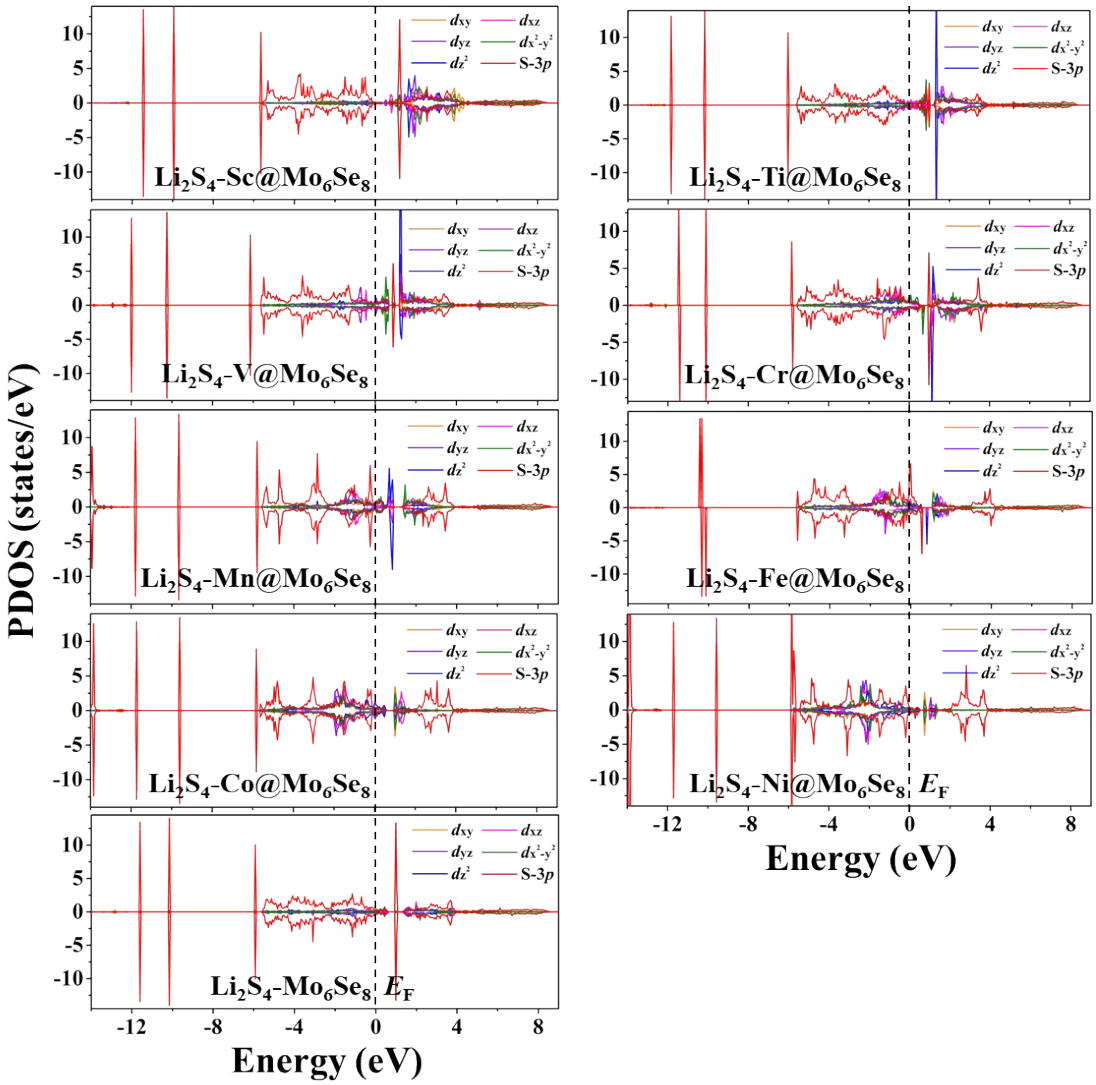
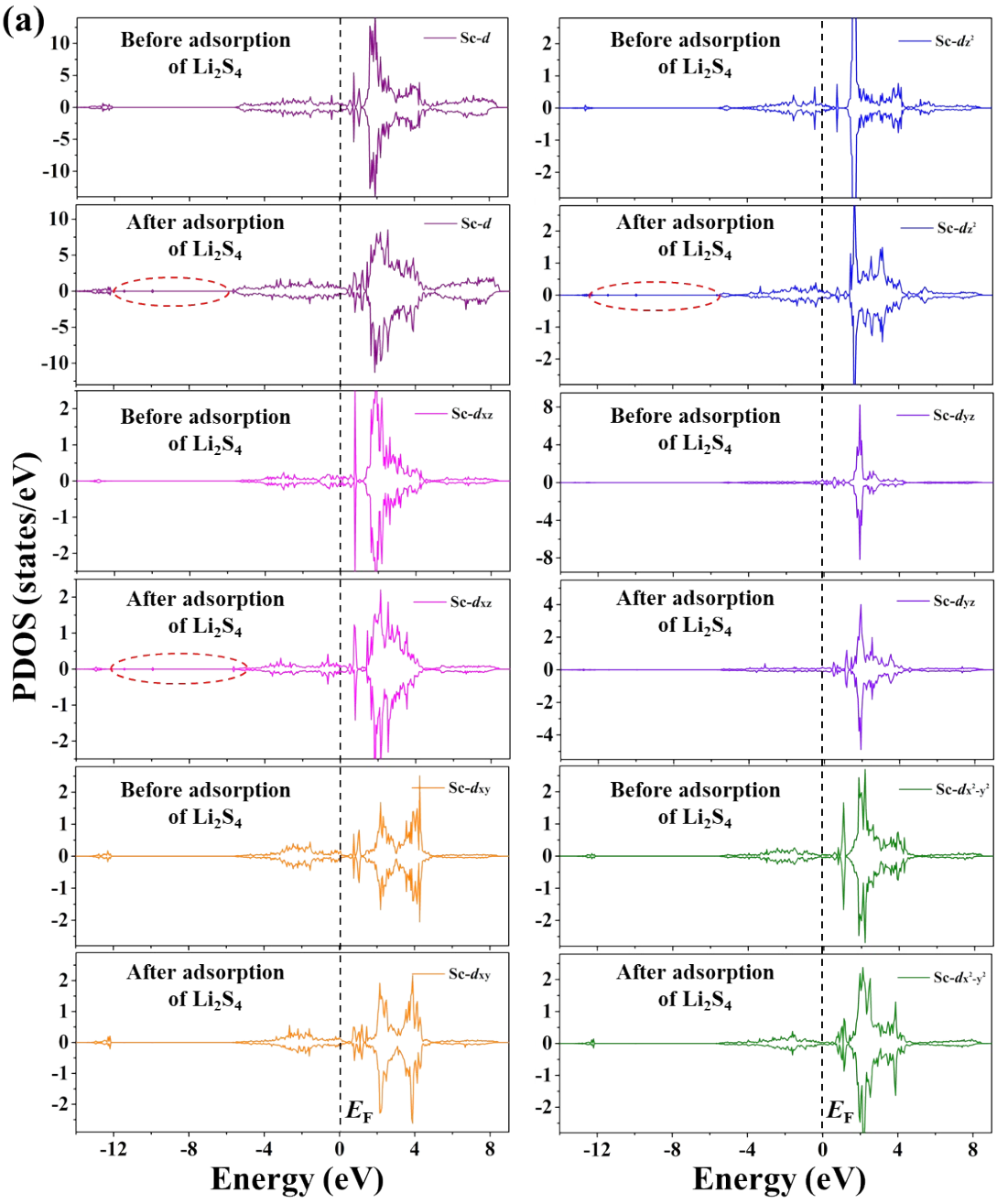
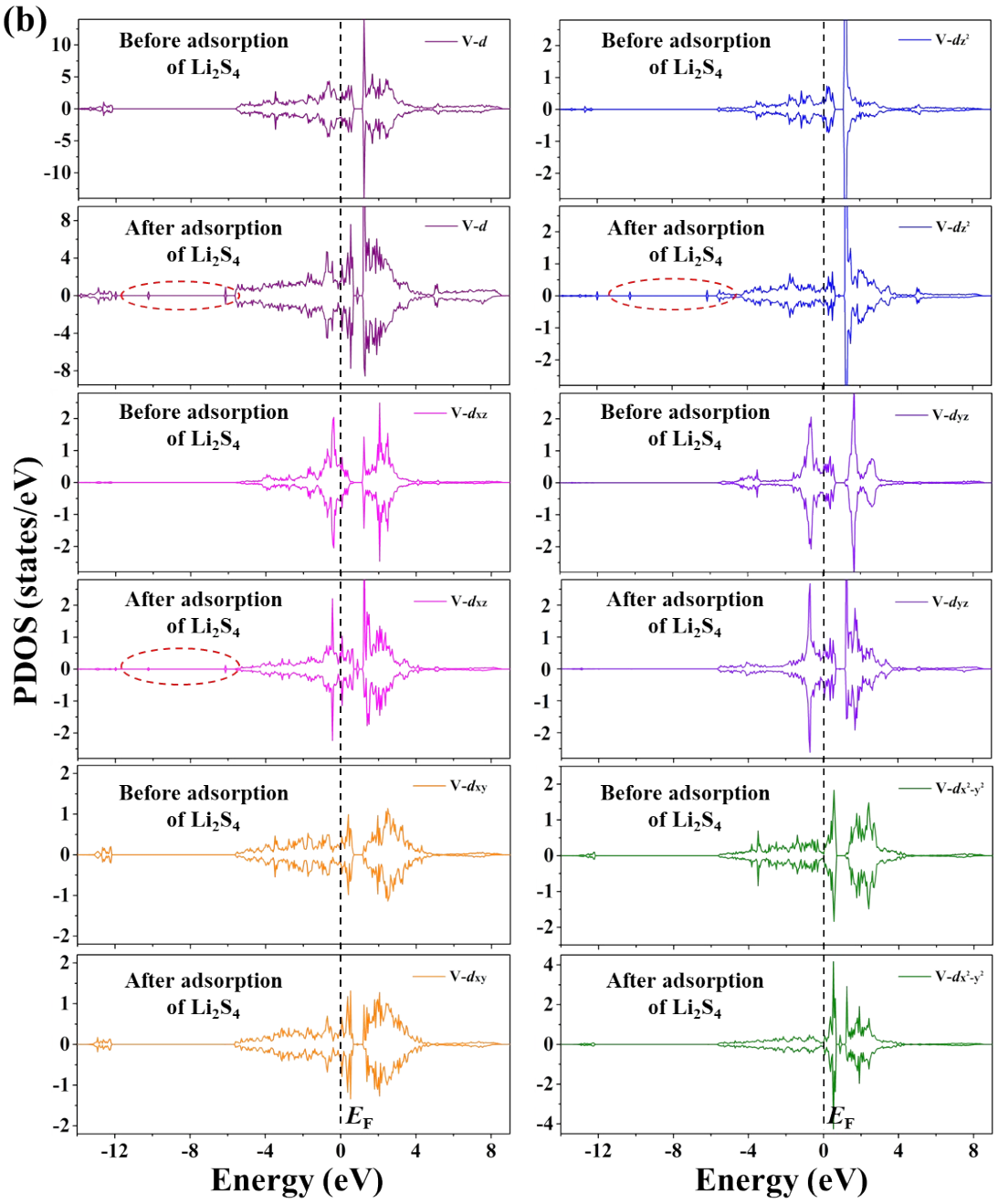
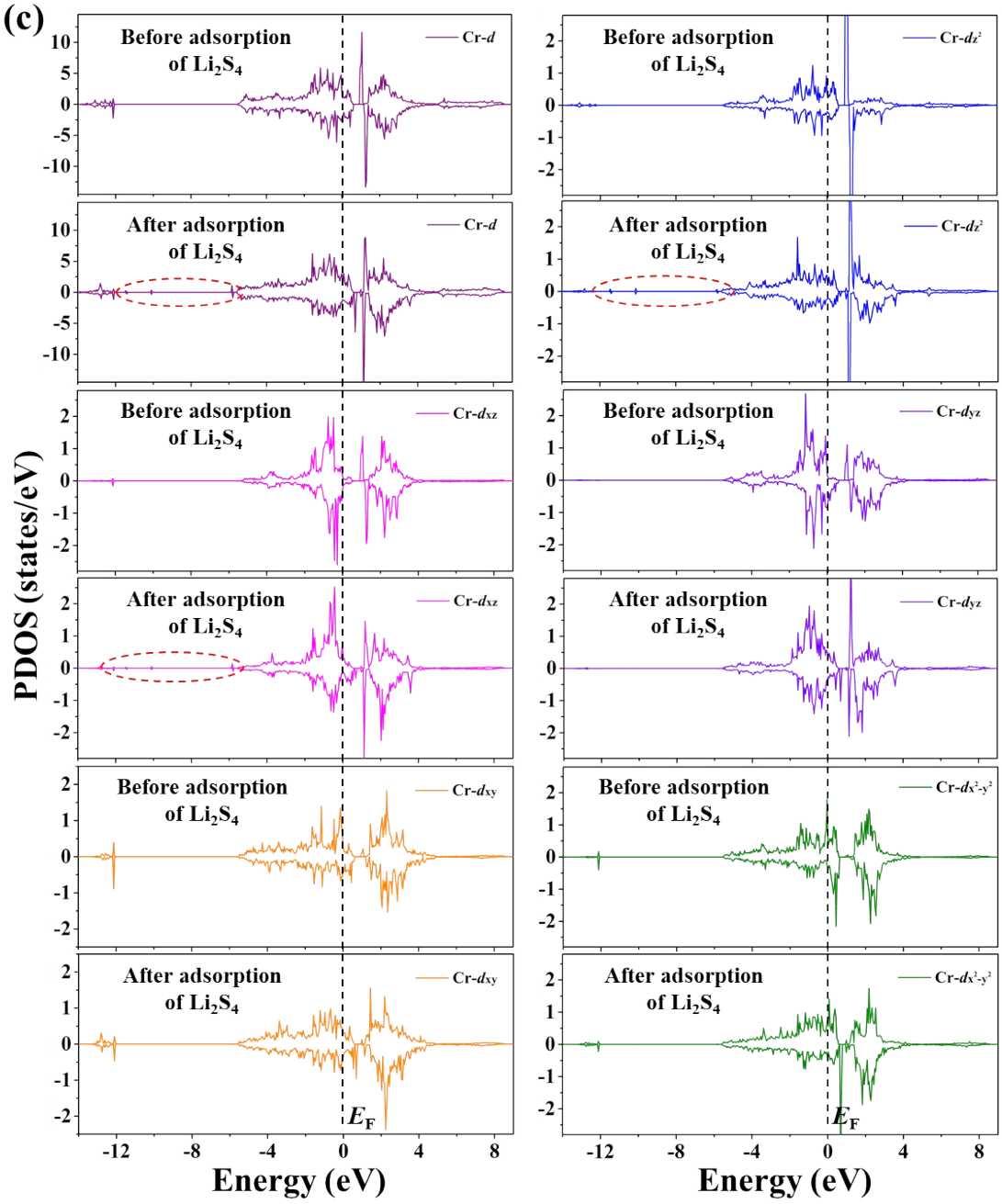


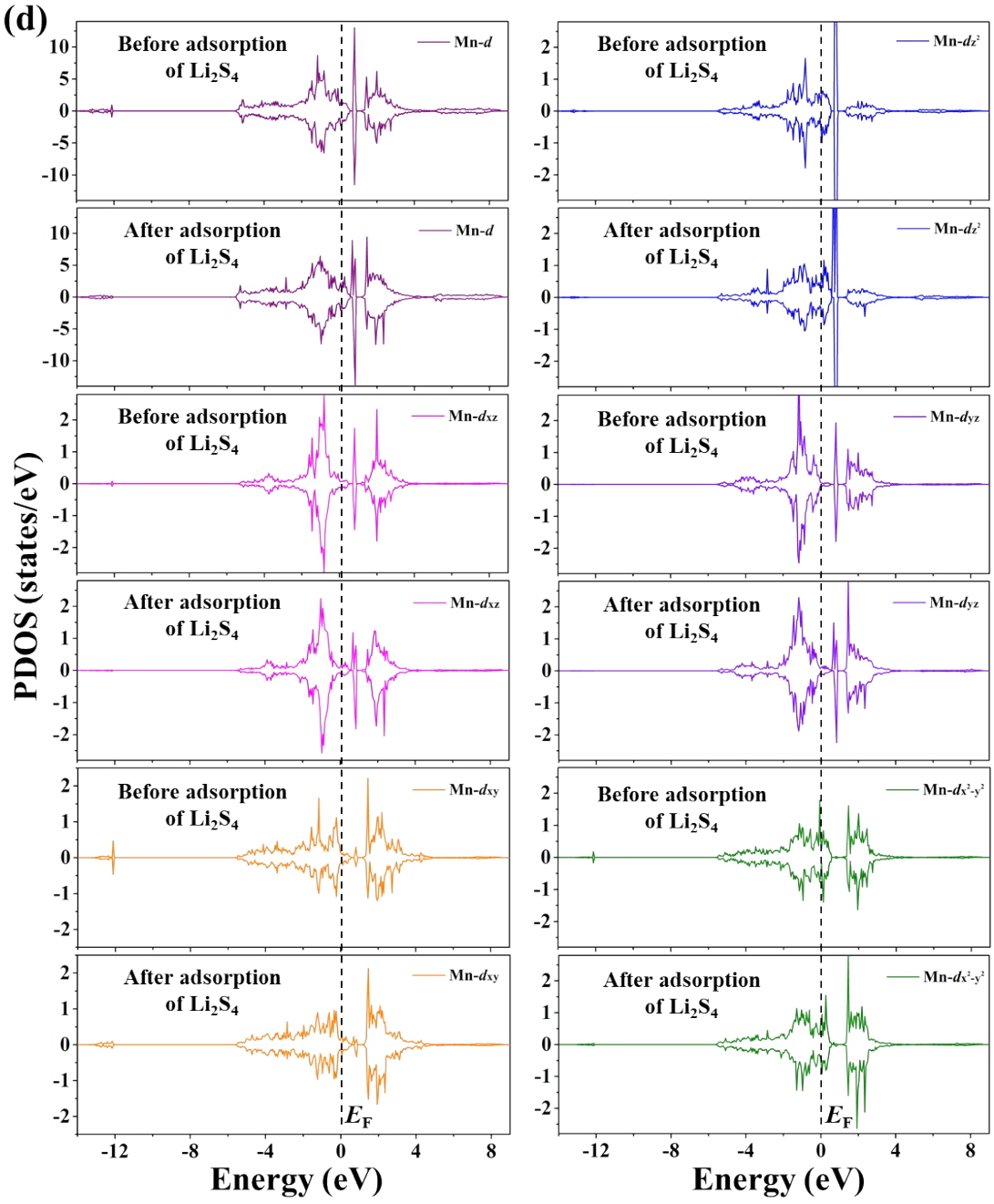
Figure S3. The projected density of states of Mo_6Se_8 and $M@Mo_6Se_8$ systems after Li_2S_4 adsorption

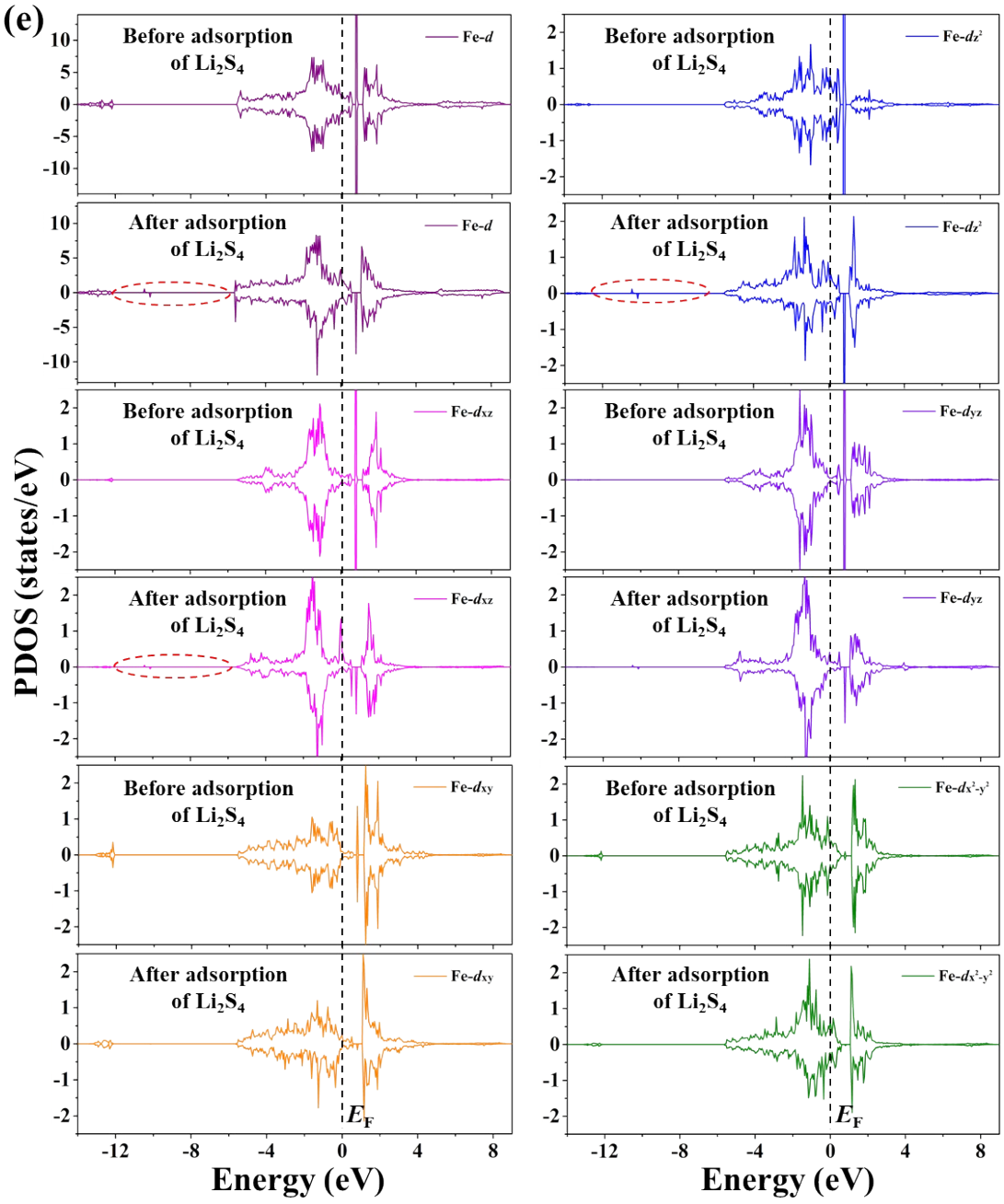
1.4 Changes of PDOS for total d orbitals and its five partial orbitals

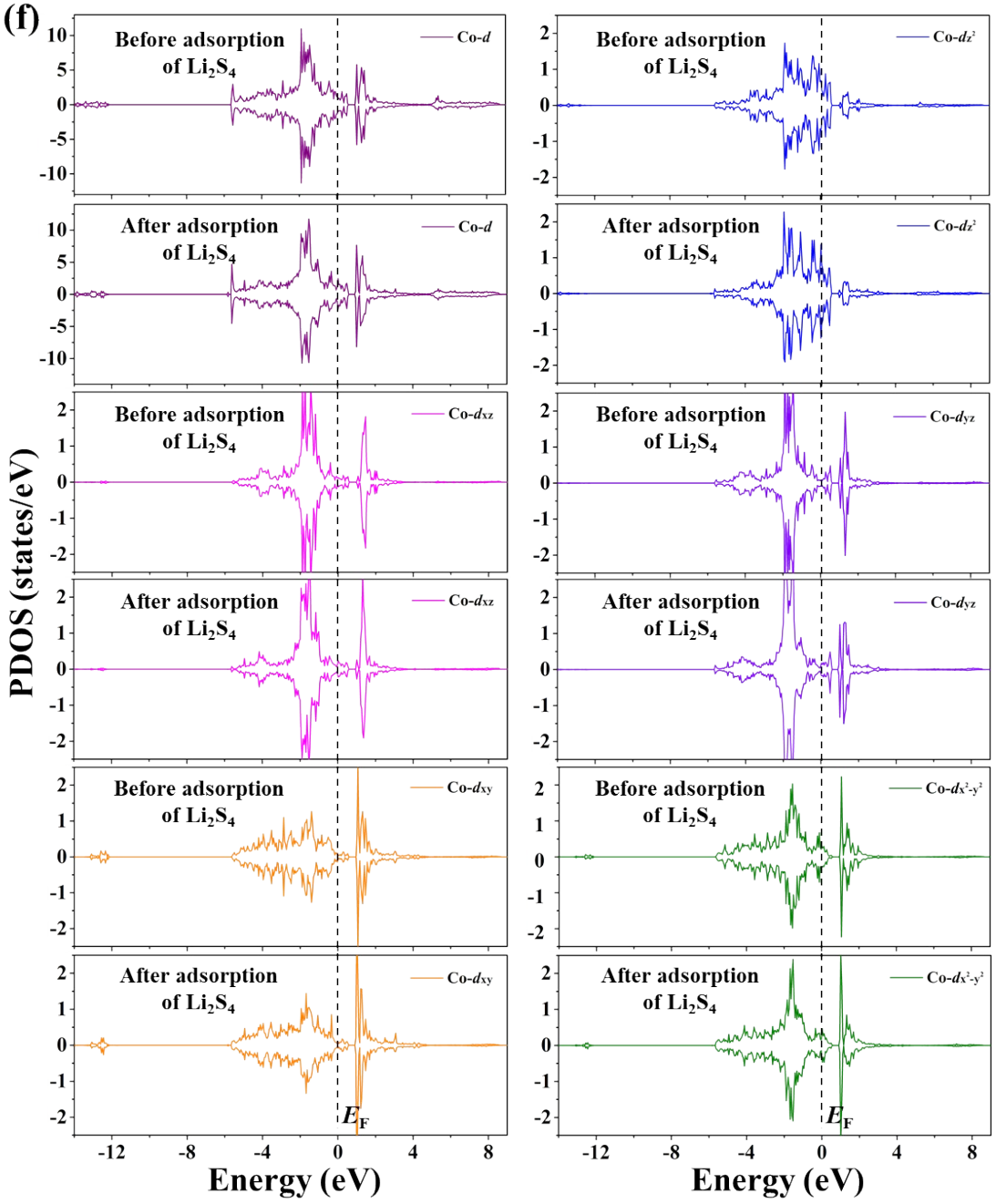


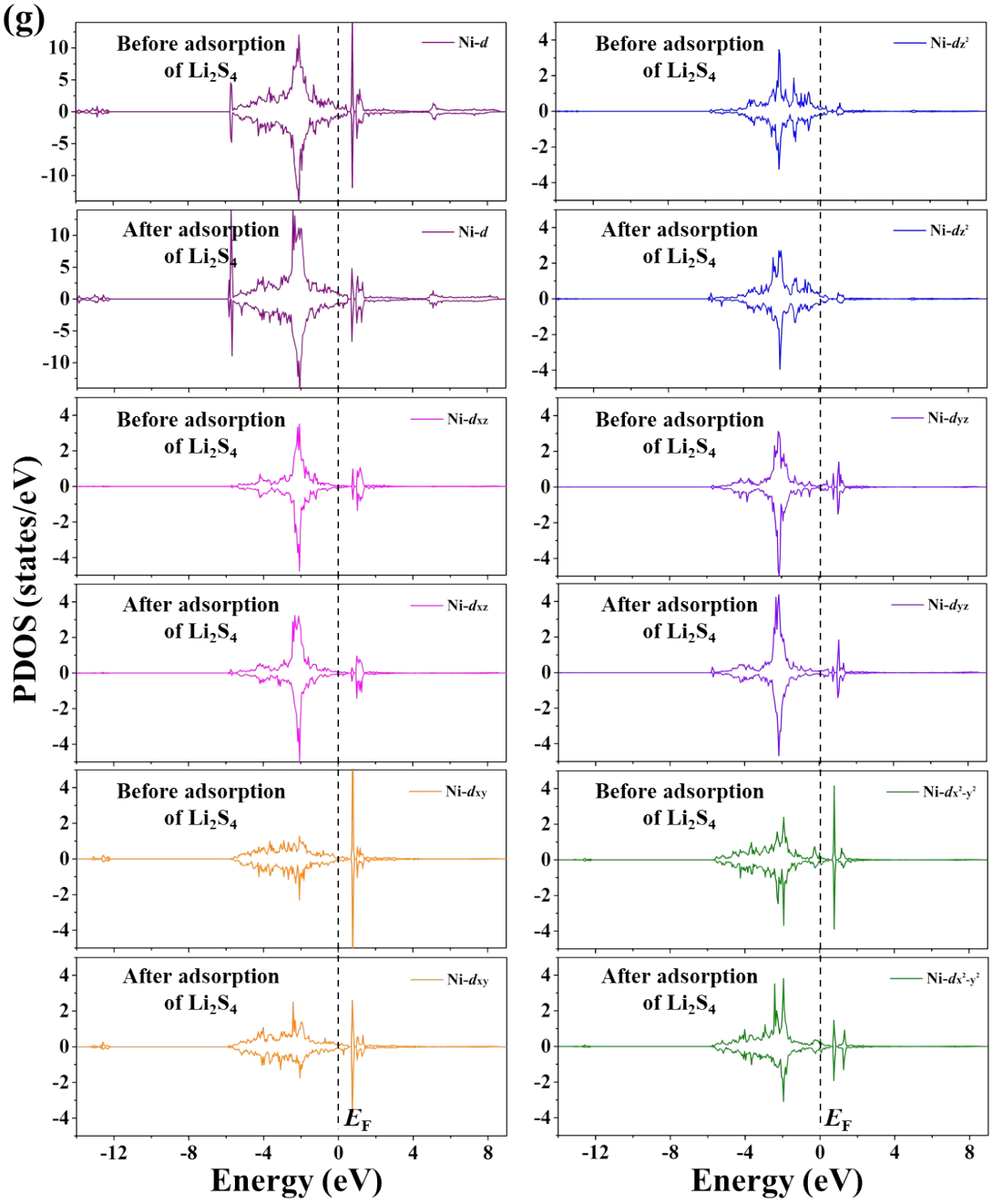

(b)
Before adsorption of Li2S4
V-d
After adsorption of Li2S4
V-d
Before adsorption of Li2S4
V-dz2
After adsorption of Li2S4
V-dz2
Before adsorption of Li2S4
V-dxz
After adsorption of Li2S4
V-dxz
Before adsorption of Li2S4
V-dyz
After adsorption of Li2S4
V-dyz
Before adsorption of Li2S4
V-dxy
After adsorption of Li2S4
V-dxy
Before adsorption of Li2S4
V-dx2-y2
After adsorption of Li2S4
V-dx2-y2
PDOS (states/eV)
EF
EF
Energy (eV)
Energy (eV)


(c)
Before adsorption of Li2S4
After adsorption of Li2S4
Cr-d
Cr-dz2
Cr-dxz
Cr-dyz
Cr-dxy
Cr-dx2-y2
PDOS (states/eV)
Energy (eV)
EF


(d)
Before adsorption of Li2S4
After adsorption of Li2S4
Mn-d
Mn-dz2
Mn-dxz
Mn-dyz
Mn-dxy
Mn-dx2-y2
PDOS (states/eV)
EF
Energy (eV)


(e)
Before adsorption of Li2S4
After adsorption of Li2S4
Fe-d
Fe-dz2
Fe-dxz
Fe-dyz
Fe-dxy
Fe-dx2-y2
PDOS (states/eV)
Energy (eV)
EF


(f)
PDOS (states/eV)
Before adsorption of Li2S4
After adsorption of Li2S4
Co-d
Co-dz2
Co-dxz
Co-dyz
Co-dxy
Co-dx2-y2
EF
Energy (eV)


(g)
Before adsorption of Li_2S_4
After adsorption of Li_2S_4
Ni-d
Ni-dz^2
Ni-dxz
Ni-dyz
Ni-dxy
Ni-dx^2-y^2
PDOS (states/eV)
E_F
Energy (eV)

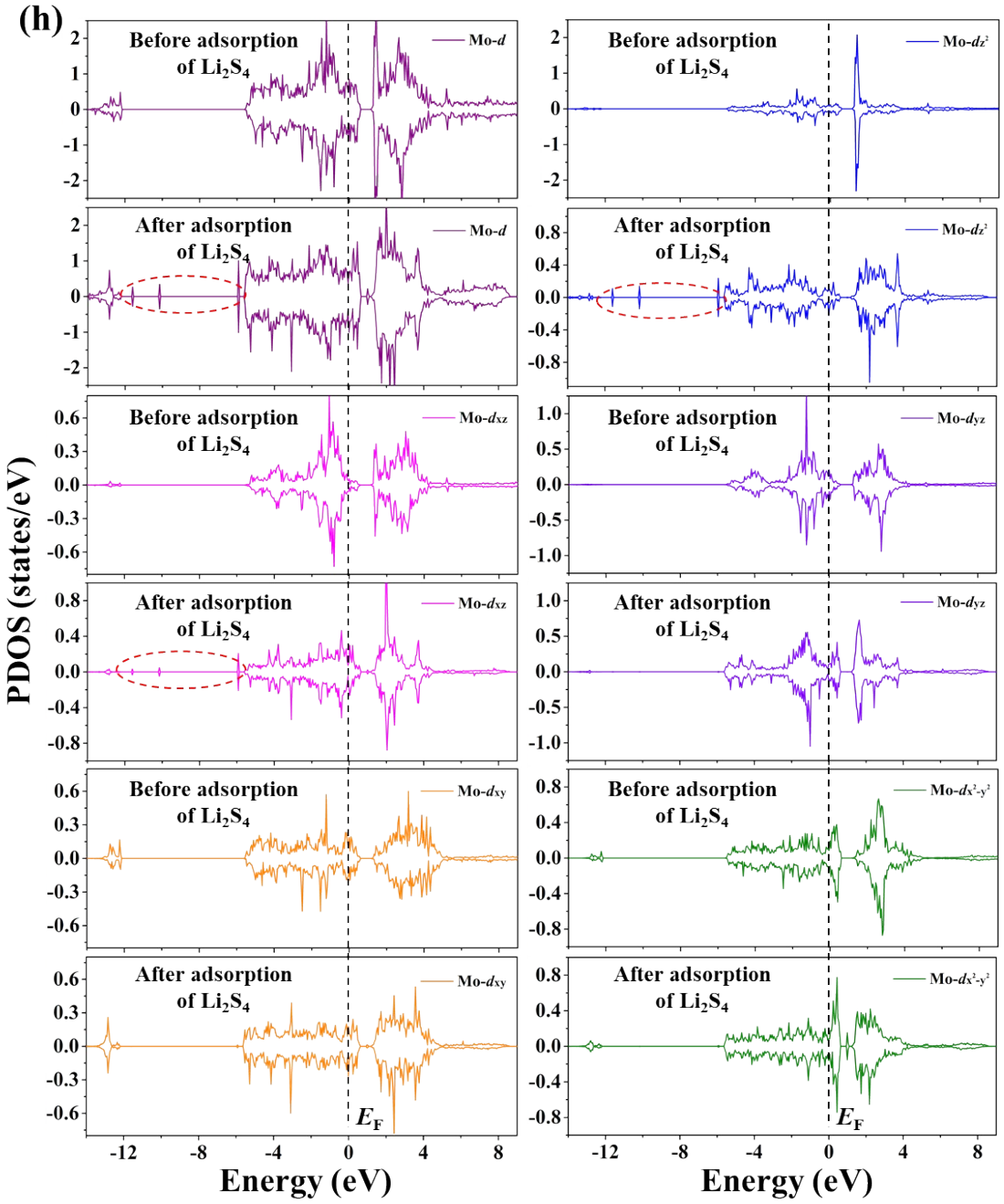
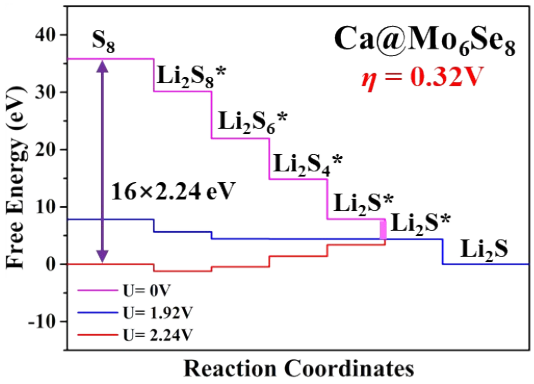
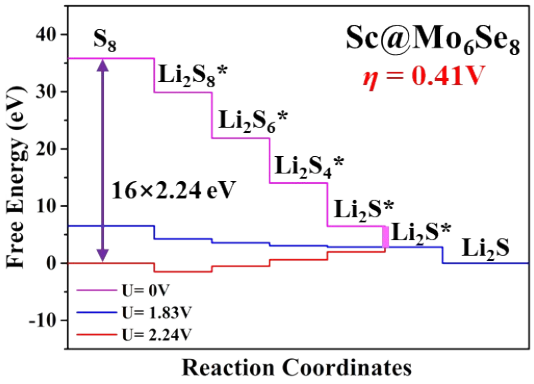
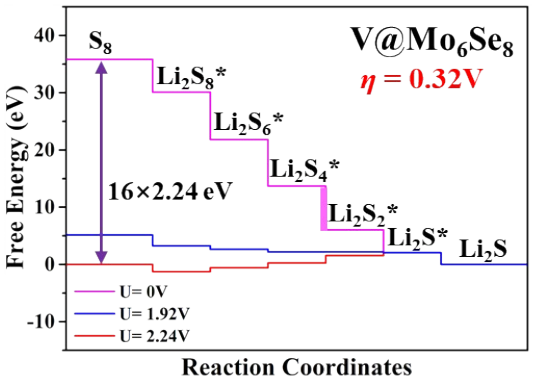


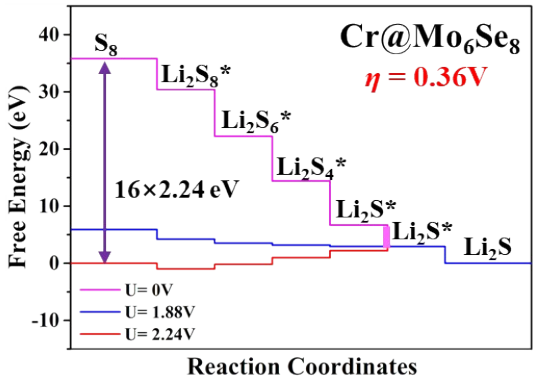
Figure S4. The changes of total d orbitals and its five components (d_z^2, d_{xz}, d_{yz}, d_x^2-$_y^2$ and d_{xy}) orbitals of doped metal before and after Li_2S_4 adsorption for (a) Sc@Mo_6Se_8 (b) V@Mo_6Se_8 (c) Cr@Mo_6Se_8 (d) Mn@Mo_6Se_8 (e) Fe@Mo_6Se_8 (f) Co@Mo_6Se_8 (g) Ni@Mo_6Se_8 (h) Mo_6Se_8 systems.

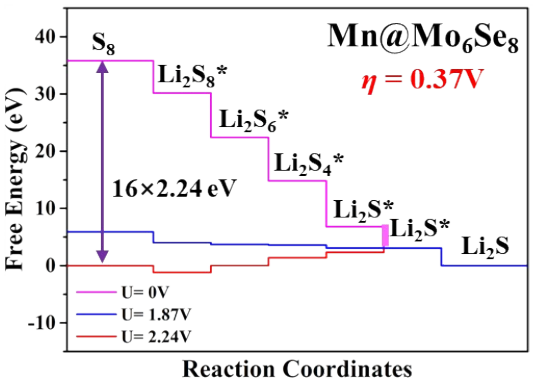
1.5 Gibbs free energy plots of SRR process

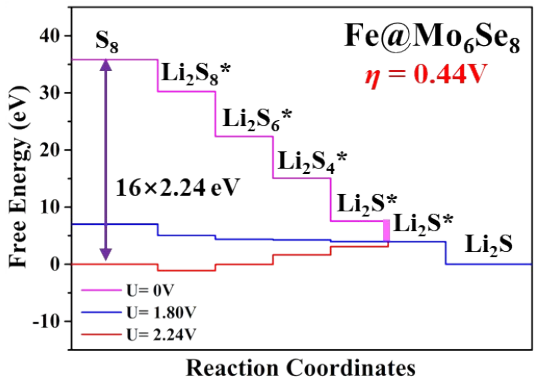












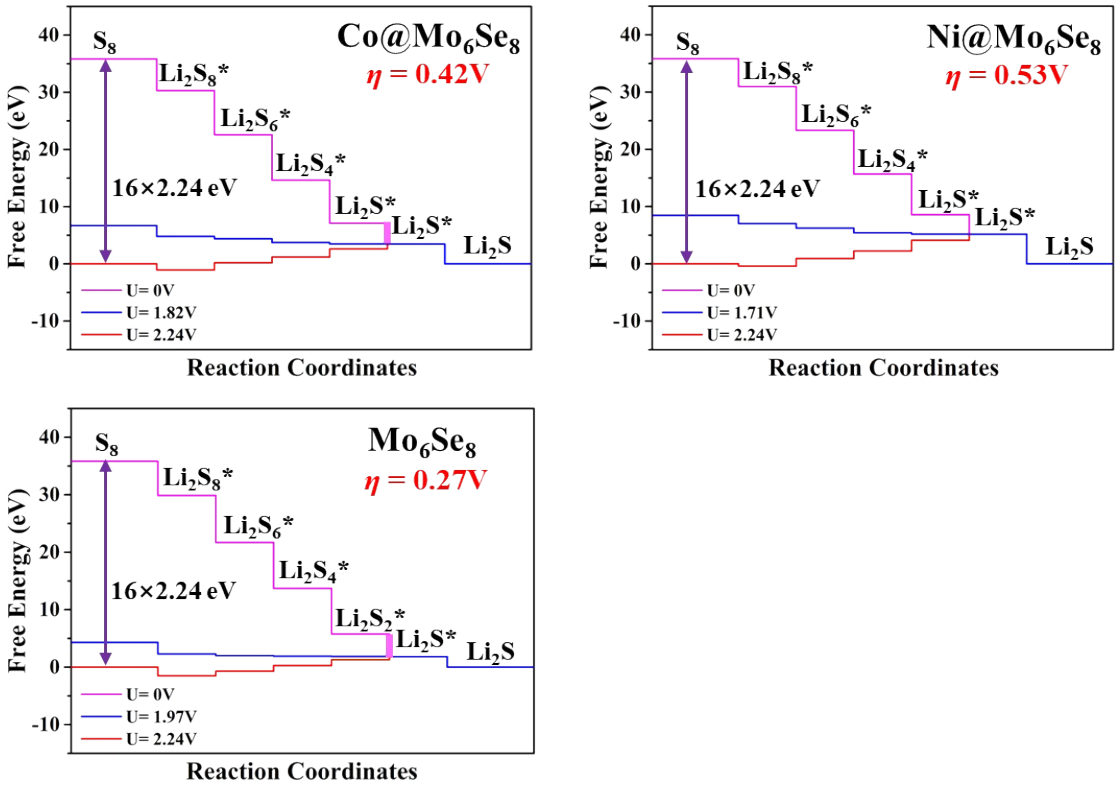


Figure S5. Gibbs free energy plots of SRR at U = 0 V, limiting potential and equilibrium potential (U = 2.24 V) for Mo_6Se_8 and $M@Mo_6Se_8$ (M = Ca, Sc, V, Mn, Fe, Co and Ni) systems.

1.6 Tests for solvation effects

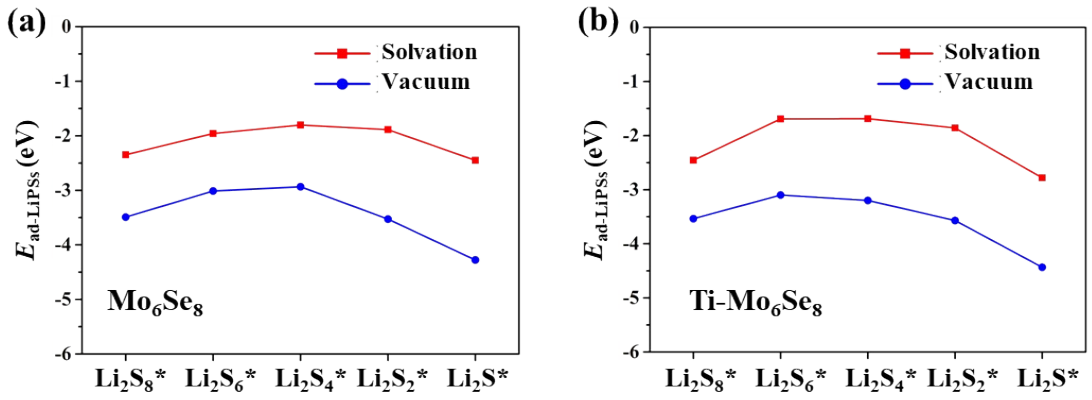


Figure S6. (a) Trends in adsorption energies of LiPSs on Mo_6Se_8 in vacuum environments and solvation effects (b) Trends in adsorption energies of LiPSs on Ti-Mo_6Se_8 in vacuum environments and solvation effects

1.7 Table S1 ~ S3

Table S1 Experimental and calculated values of lattice constants of Mo_6Se_8

Material	Unit Cell Parameter	Experimental Value (Å)	Calculated Value (Å)	|% Difference|
Mo_6Se_8	a	6.66[1]	6.63	0.45
	b	6.66	6.61	0.75
	c	6.66	6.64	0.30
	α	91.70	91.49	0.23
	β	91.70	91.56	0.15
	γ	91.70	91.41	0.32

Table S2. Descriptors of metal-doped Mo_6Se_8 and Mo_6Se_8 systems (see footnotes for definitions of each descriptor).

Systems	η (V)	ε_d (eV)	d_n (eV)	W (eV)	Q_m (e)	r_d (Å)	A_m (eV)	I_m (eV)	N_m
Sc@Mo_6Se_8	0.41	1.68	3	4.88	-2.87	1.44	0.19	6.56	1.36
Ti@Mo_6Se_8	0.21	0.94	4	4.89	-2.53	1.32	0.08	6.83	1.54
V@Mo_6Se_8	0.32	0.40	5	4.97	-1.98	1.22	0.53	5.75	1.63
Cr@Mo_6Se_8	0.36	0.44	6	5.15	-1.43	1.18	0.68	6.77	1.66
Mn@Mo_6Se_8	0.37	-0.22	7	5.20	-0.96	1.17	-0.50	7.43	1.55
Fe@Mo_6Se_8	0.44	-0.46	8	5.19	-0.63	1.17	0.15	7.90	1.83
Co@Mo_6Se_8	0.42	-1.31	9	5.14	-0.39	1.16	0.66	7.88	1.88
Ni@Mo_6Se_8	0.62	-1.94	10	5.11	-0.30	1.15	1.16	7.64	1.91
Mo_6Se_8	0.27	0.13	6	5.01	-1.48	1.30	0.75	7.09	2.16

ε_d is the d band center the doped metal from −6 eV to 6 eV

d_n is the number of valence electrons of the doped metal atom

W is the work function of the catalyst

Q_m is the bader charge transfer number of the doped metal atom, negative values represent loss of electrons

N_m is electronegativity of doped metal atom

A_m is the electron affinity energy of doped metal atom

I_m is the first ionization energy of doped metal atom

r_d is the atomic radius of the doped metal

Table S3. The correction of zero-point energy and entropy of adsorption species and molecules involved in SRR. *T* is the room temperature (298.15 K) and * denotes the active site on the catalyst surface.

Systems		Li_2S_8*	Li_2S_6*	Li_2S_4*	Li_2S_2*	Li_2S*
Ca@Mo_6Se_8	ZPE	0.82	0.68	0.49	0.35	0.29
	TS	1.89	1.46	1.10	0.71	0.47
Sc@Mo_6Se_8	ZPE	0.82	0.64	0.47	0.36	0.26
	TS	1.91	1.52	1.13	0.67	0.52
Ti@Mo_6Se_8	ZPE	0.81	0.64	0.46	0.35	0.26
	TS	1.92	1.38	1.12	0.70	0.52
V@Mo_6Se_8	ZPE	0.83	0.63	0.46	0.35	0.26
	TS	1.87	1.52	1.13	0.68	0.49
Cr@Mo_6Se_8	ZPE	0.80	0.65	0.46	0.35	0.26
	TS	1.83	1.50	1.15	0.70	0.53
Mn@Mo_6Se_8	ZPE	0.84	0.63	0.46	0.35	0.26
	TS	1.86	1.52	1.19	0.70	0.51
Fe@Mo_6Se_8	ZPE	0.84	0.64	0.48	0.35	0.26
	TS	1.87	1.54	1.19	0.70	0.52
Co@Mo_6Se_8	ZPE	0.84	0.62	0.50	0.35	0.26
	TS	1.86	1.43	1.12	0.72	0.51
Ni@Mo_6Se_8	ZPE	0.81	0.63	0.50	0.35	0.26
	TS	1.94	1.53	1.12	0.72	0.52
Mo_6Se_8	ZPE	0.82	0.63	0.48	0.32	0.27
	TS	1.89	1.50	1.12	0.70	0.48

1.8 References

[1] G. Concas, F. Congiu, A. G. Lehmann, C. Muntoni, S. Sanna, G. Spano, *Z NATURFORSCH A*, 2002, **57**, 221.