Supplementary information

Theoretical identifying the superior anchoring effect and electrochemical performance of Ti2CS2 by single atom Zn doping for lithium-sulfur batteries

Mingyang Wang[1,2], Jianjun Mao[3] Yudong Pang[1], Xilin Zhang[1], Haiyan Wang[4], Zongxian Yang[1*], Zhansheng Lu[1*] and Shuting Yang[2*]

[1]*School of Physics, Henan Normal University and Henan Key Laboratory of Photovoltaic Materials, Xinxiang, Henan, 453007, People's Republic of China*

[2] *Henan Battery Research Institute, Xinxiang, Henan, 453007, People's Republic of China*

[3] *Department of Chemistry, The University of Hong Kong, Pok Fu Lam Road, Hong Kong, People's Republic of China*

[4]*Collaborative Innovation Centre of Henan Province for Green Manufacturing of Fine Chemicals, Key Laboretory of Green Chemical Media and Reactions, Ministry and Chemistry Engineering, Henan Normal University, Xinxiang, Henan, 453007, China.*

**Authors to whom correspondence should be addressed: yzx@htu.edu.cn (ZY); zslu@htu.edu.cn (ZL) and yangshuting17@163.com (SY)*

COMPUTATIONAL DETAILS

To guarantee that the supercell size of the surface model was sufficiently large to avoid the effect of surface functional groups and LiPS's between their mirror images in the *x*-*y* plane on the surface, the calculations were performed with a 3 × 3 × 1 supercell. The supercell integration is sampled with a 4 × 4 × 1 k-point mesh generated via the Monkhorst–Pack scheme. To avoid direct interaction between the periodic images, a vacuum spacing of 20 Å in the *z*-direction normal to the surface was used. The Climbing Image Nudged Elastic Band (CI-NEB) method with four images is used to search for saddle points and minimum energy paths on potential energy surfaces between reactants and products. The phonon calculations are carried out by using the Phononpy code, and the real-space force constants were calculated using density-functional perturbation theory (DFPT) as implemented in VASP. Moreover, a more strict energy (10^{-8} eV per atom) and force convergence criterion (10^{-4} eV/ Å) were used during the vibration spectra calculations. To test the thermal stabilities of the monolayer, the AIMD simulations were performed in a canonical ensemble (NVT). In the MD calculations, the temperature was kept at 300 K for 10 ps with a time step of 1 fs. To study the adsorption stability, the adsorption energies has been calculated using a formula of:

$E_{ads} = E_{sub} + E_{ad} - E_{ad/sub}$ (1)

where E_{sub}, E_{ad} and $E_{ad/sub}$ are the calculated total energies of the optimized MXenes or electrolyte molecules, the optimized adsorbate in the gas phase, and the adsorbate–substrate system, respectively. Since transition metal (TM) vacancies can be easily formed during the experimental synthesis process of MXene, we chose the defected Ti_2CS_2 MXene with a TM vacancy as a parent system to construct a single Zn doped Ti_2CS_2 system (denoted by $Ti_{2-x}Zn_xCS_2$). The formation energy is defined by the following formula：

$E_{fomation\ energy} = E_{defect\ system} + E_{doping\ atom} - E_{doped\ system}$ (2),

where $E_{defect\ system}$, $E_{doping\ atom}$ and $E_{doped\ system}$ are the total energies of the supercell with a TM atomic vacancy, a single doping atom (the energy per TM atom in bulk TM metal, for example, if the doping atom is Zn, the $E_{doping\ atom}$ is the energy per Zn atom in bulk Zn metal) and the doped supercell, respectively. The calculated doping formation energy for the $Ti_{2-x}Zn_xCS_2$ systems is 3.07 eV, which implied thermodynamically favorable of the single Zn doped structures.

STRUCTURE INFORMATION

$Ti_{2-x}Zn_xCS_2$

1.00000000000000

8.2608559376187287 -4.7694028098524965 0.0000000000000000
0.0000000000000000 9.5388056197049949 0.0000000000000000
0.0000000000000000 0.0000000000000000 22.0544038665421169
S C Ti Zn
18 9 17 1
Selective dynamics
Direct

0.2234590072332403	0.1099764992248873	0.3743842796582812	T	T	T
0.1107483836525828	0.2220408584929593	0.6250228299218660	T	T	T
0.5531841586582901	0.1099764992248873	0.3743842796582812	T	T	T
0.4393903716297269	0.2121140765927826	0.6274776997004563	T	T	T
0.8888888888888857	0.1111111111111143	0.3731679071724587	T	T	T
0.7779591415070408	0.2220408584929593	0.6250228299218660	T	T	T
0.2234590072332403	0.4468158413417029	0.3743842796582812	T	T	T
0.1122940484679357	0.5579214302691929	0.6257976385658122	T	T	T
0.5555555555555571	0.4444444444444429	0.3763471532618203	T	T	T
0.4393903716297269	0.5606096283702731	0.6274776997004563	T	T	T
0.8900235007751126	0.4468158413417029	0.3743842796582812	T	T	T
0.7878859234072175	0.5606096283702731	0.6274776997004563	T	T	T
0.2222222222222214	0.7777777777777786	0.3747913236548634	T	T	T
0.1122940484679357	0.8877059515320643	0.6257976385658122	T	T	T
0.5531841586582901	0.7765409927667597	0.3743842796582812	T	T	T
0.4420785697308071	0.8877059515320643	0.6257976385658122	T	T	T
0.8900235007751126	0.7765409927667597	0.3743842796582812	T	T	T
0.7779591415070408	0.8892516163474172	0.6250228299218660	T	T	T
0.9998284223839907	0.0001715776160093	0.4996173250194798	T	T	T
0.3341604590991733	0.0016542515316609	0.5004503396074260	T	T	T
0.6670098218986759	0.0001715776160093	0.4996173250194798	T	T	T
0.9998284223839907	0.3329901781013241	0.4996173250194798	T	T	T
0.3239204833459028	0.3286269083396228	0.4985356473843406	T	T	T
0.6713730916603772	0.3286269083396228	0.4985356473843406	T	T	T
0.9983457484683390	0.6658395409008268	0.5004503396074260	T	T	T
0.3341604590991733	0.6658395409008268	0.5004503396074260	T	T	T
0.6713730916603772	0.6760795166540972	0.4985356473843406	T	T	T
0.2222132702946566	0.1117253751248145	0.5548834822947359	T	T	T
0.1124602330326111	0.2228967831829663	0.4438237796605365	T	T	T
0.5561787714968293	0.1117253751248145	0.5548834822947359	T	T	T
0.4454472567992693	0.2242278469318956	0.4465994551215307	T	T	T
0.8888888888888857	0.1111111111111143	0.5535426343754690	T	T	T
0.7771032168170336	0.2228967831829663	0.4438237796605365	T	T	T
0.2222132702946566	0.4438212285031707	0.5548834822947359	T	T	T
0.1111323944059106	0.5555981221451356	0.4448535058465993	T	T	T
0.4454472567992693	0.5545527432007307	0.4465994551215307	T	T	T
0.8882746248751856	0.4438212285031707	0.5548834822947359	T	T	T

0.7757721530681115	0.5545527432007307	0.4465994551215307	T	T	T
0.2222222222222214	0.7777777777777786	0.5544023521123839	T	T	T
0.1111323944059106	0.8888676055940894	0.4448535058465993	T	T	T
0.5561787714968293	0.7777867297053436	0.5548834822947359	T	T	T
0.4444018778548645	0.8888676055940894	0.4448535058465993	T	T	T
0.8882746248751856	0.7777867297053436	0.5548834822947359	T	T	T
0.7771032168170336	0.8875397669673889	0.4438237796605365	T	T	T
0.5555555555555571	0.4444444444444429	0.5556073952207602	T	T	T

FIGURES

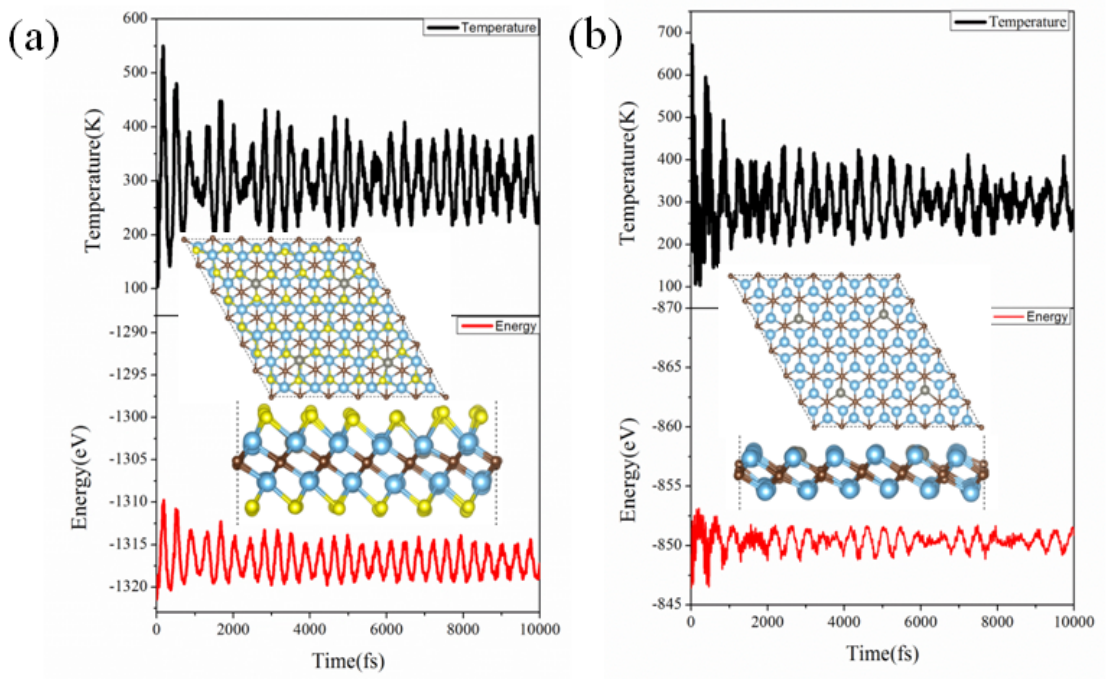

Fig. S1 (a)-(b) AIMD simulations at the temperature of 300 K lasting for 10 ps on the $Ti_{2-x}Zn_xCS_2$ and Ti_2CS_2. The insert figures are the top and side view of the $Ti_{2-x}Zn_xCS_2$ and Ti_2CS_2 at the end of simulated time.

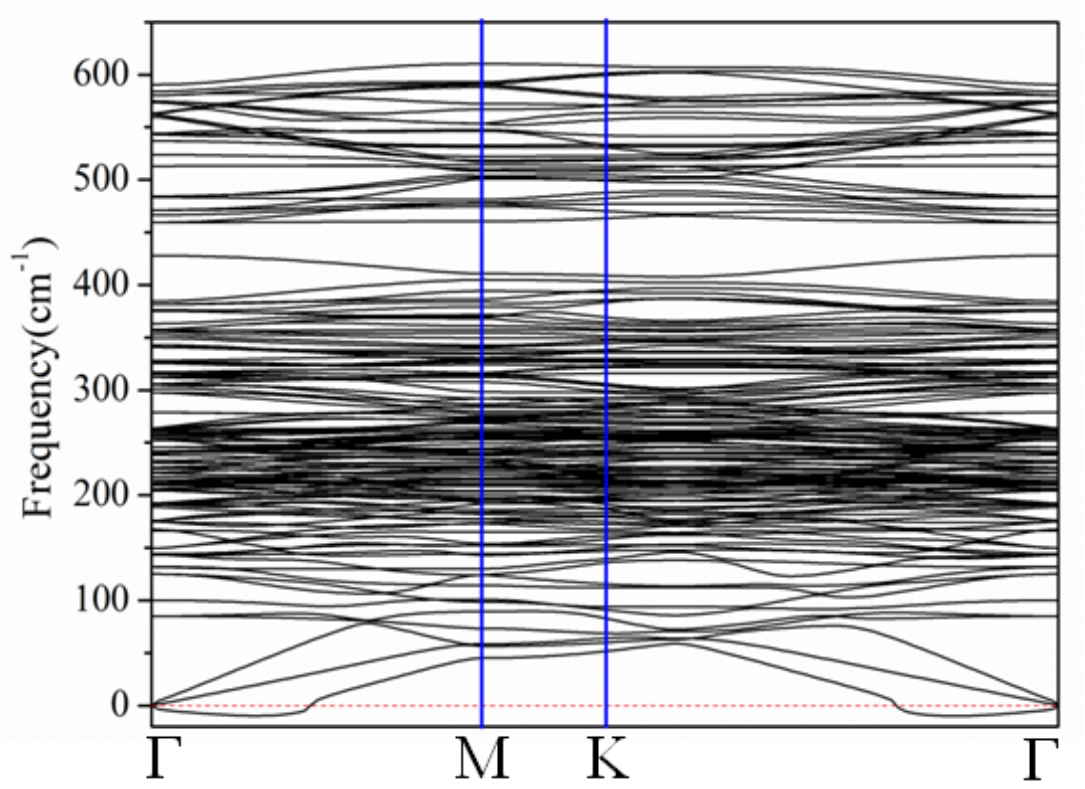

Fig. S2 The phonon dispersion spectra of pristine $Ti_{2-x}Zn_xCS_2$.

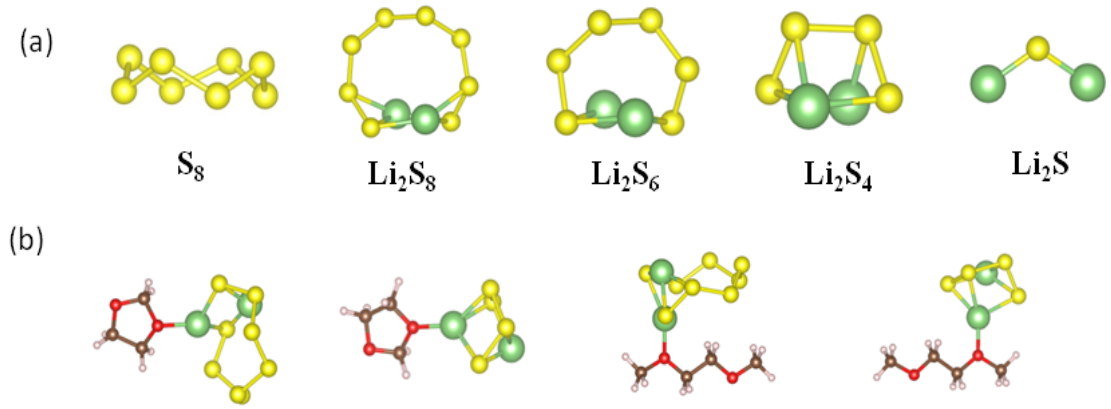

Figure S3. (a) the structures of S8 and LiPSs; (b) the optimized adsorption structures of Li2S8, Li2S4 with DOL and DME, respectively.

TABLES

Table S1. The bond length and bong angle of S_8 and LiPS's.

	S_8	Li_2S_8	Li_2S_6	Li_2S_4	Li_2S
S-S bond length(Å)	2.06	2.06	2.07	2.08	-
Li-S bond length(Å)	-	2.38	2.38	2.37	2.09
Li-S-Li bond angle(º)	-	65.5	68.8	73.3	111.8
S-S-S bond angle(º)	109.4	110.0	108.7	105.2	-
S- Li-S bond angle(º)	-	110.9	109.4	104.9	-
Adsorption energy on $Ti_{2-x}Zn_xCS_2$ (eV)	0.88	1.99	2.49	2.98	4.74

Table S2. The adsorption energy (E_{ads}, in eV) and adsorption height (h, in Å) of Li atoms at different sites (1~4) on the $Ti_{2-x}Zn_xCS_2$ Monolayer.

	1	2	3	4
E_{ads} (eV)	3.92	3.97	4.01	4.14
h (Å)	1.40	1.39	1.34	1.32