Supporting Information: Can P_3S and C_3S Monolayers be Used as Anode Materials in Metal-Ion Batteries? An Answer from First-Principles Study

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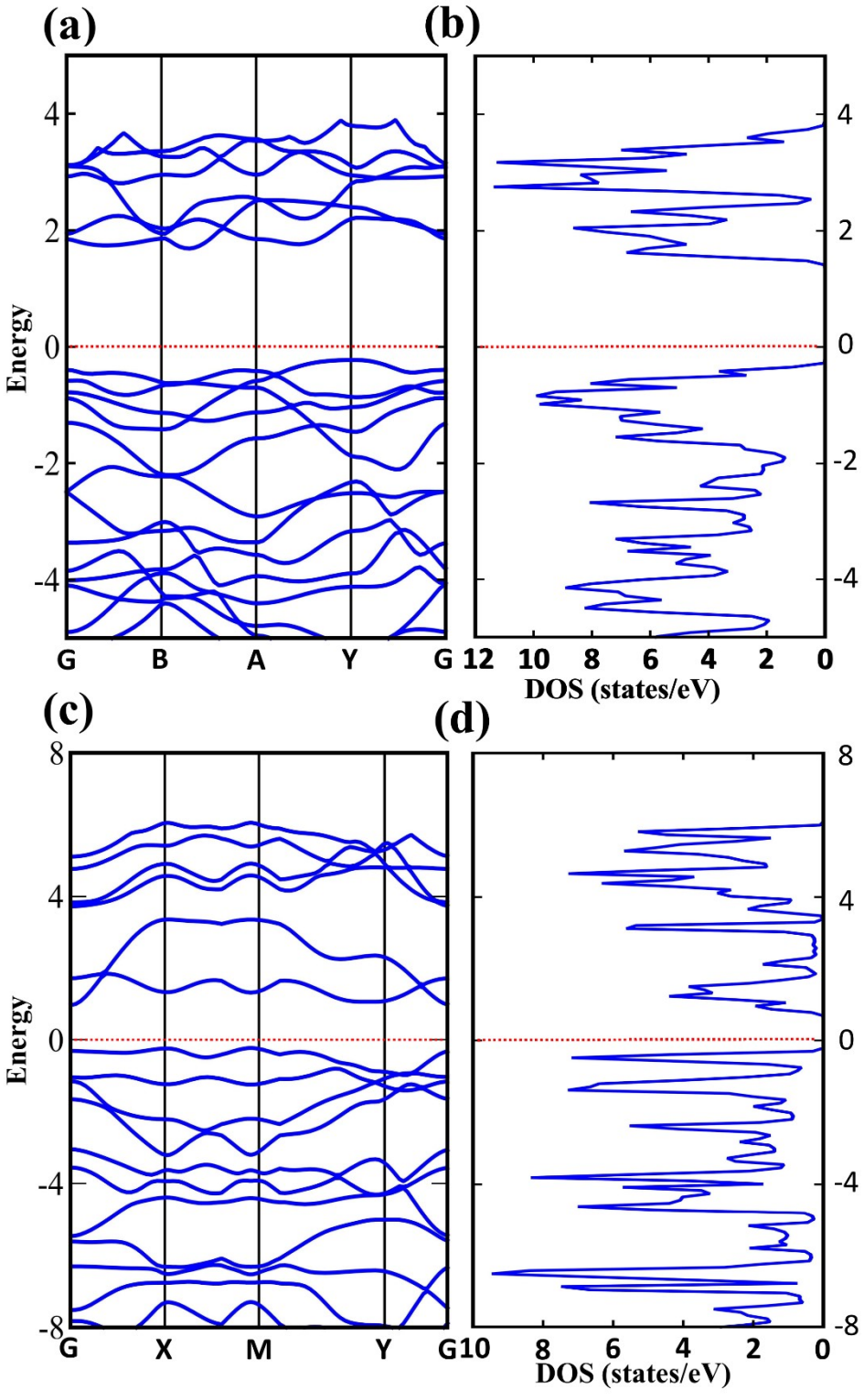

Figure S1. Electronic properties (Band structure and total density of states): pristine (a,b) P_3S and (c,d) C_3S monolayers. Fermi levels are set to zero. (PBE calculations).

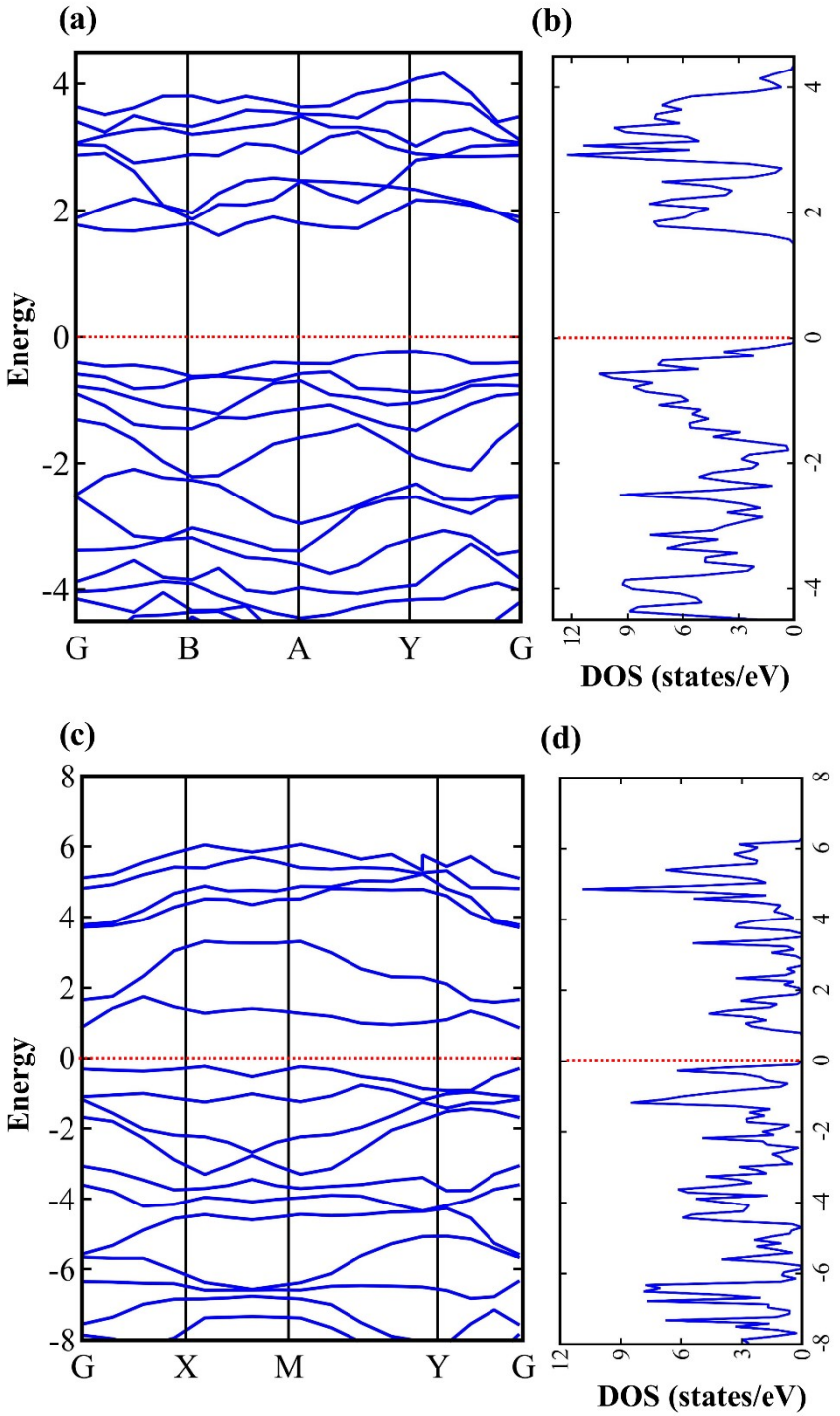

Figure S2. Electronic properties (Band structure and total density of states): pristine (a,b) P_3S and (c,d) C_3S monolayers. Fermi levels are set to zero. (PBEsol calculations).

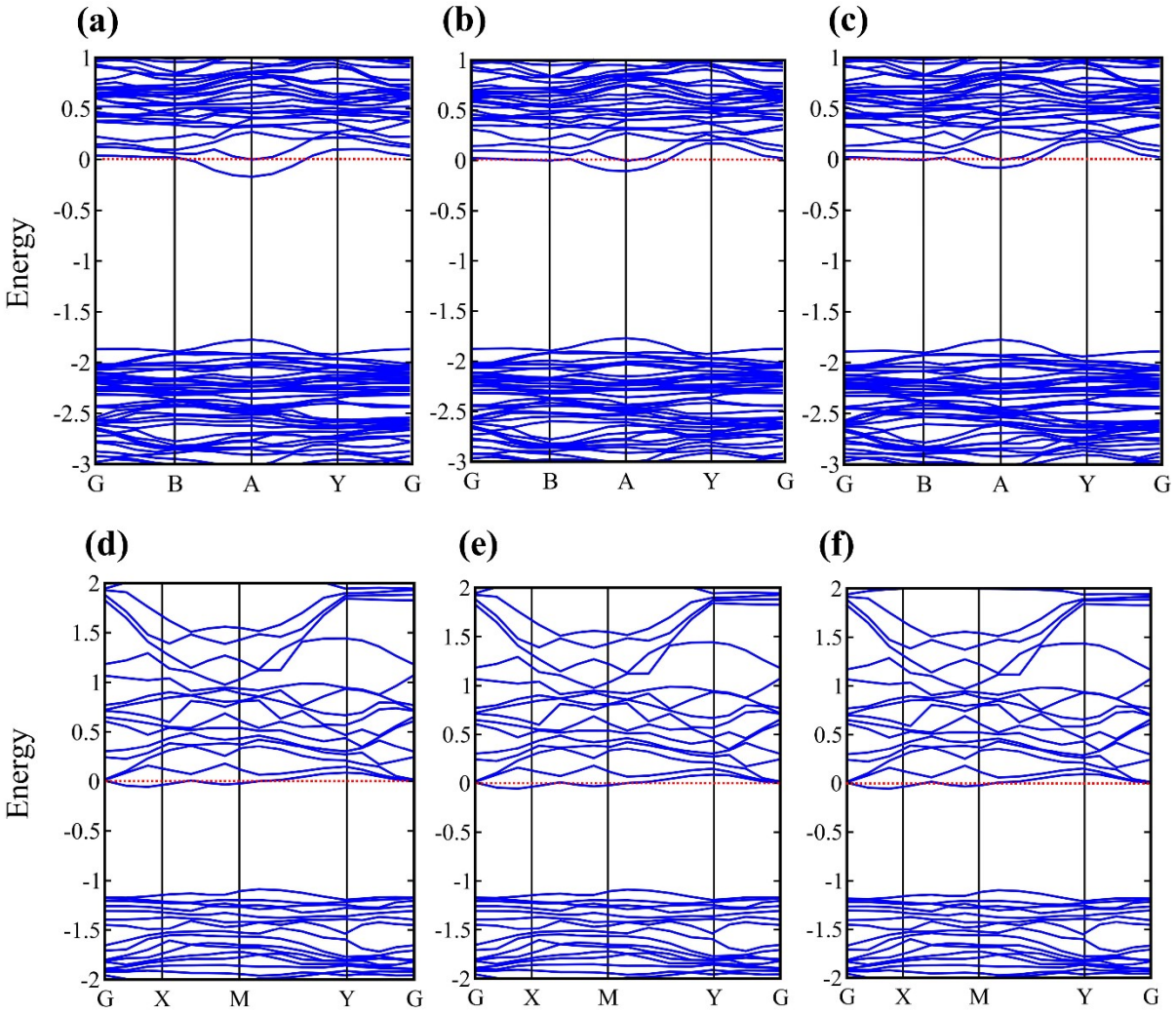

Figure S3. Electronic properties (Band structure and total density of states) of the single alkali metal adsorbed P_3S and C_3S monolayers: (a-c) and (d-f) represent Li-, Na-, and K-adsorbed P_3S and C_3S systems, respectively. Fermi levels are set to zero.

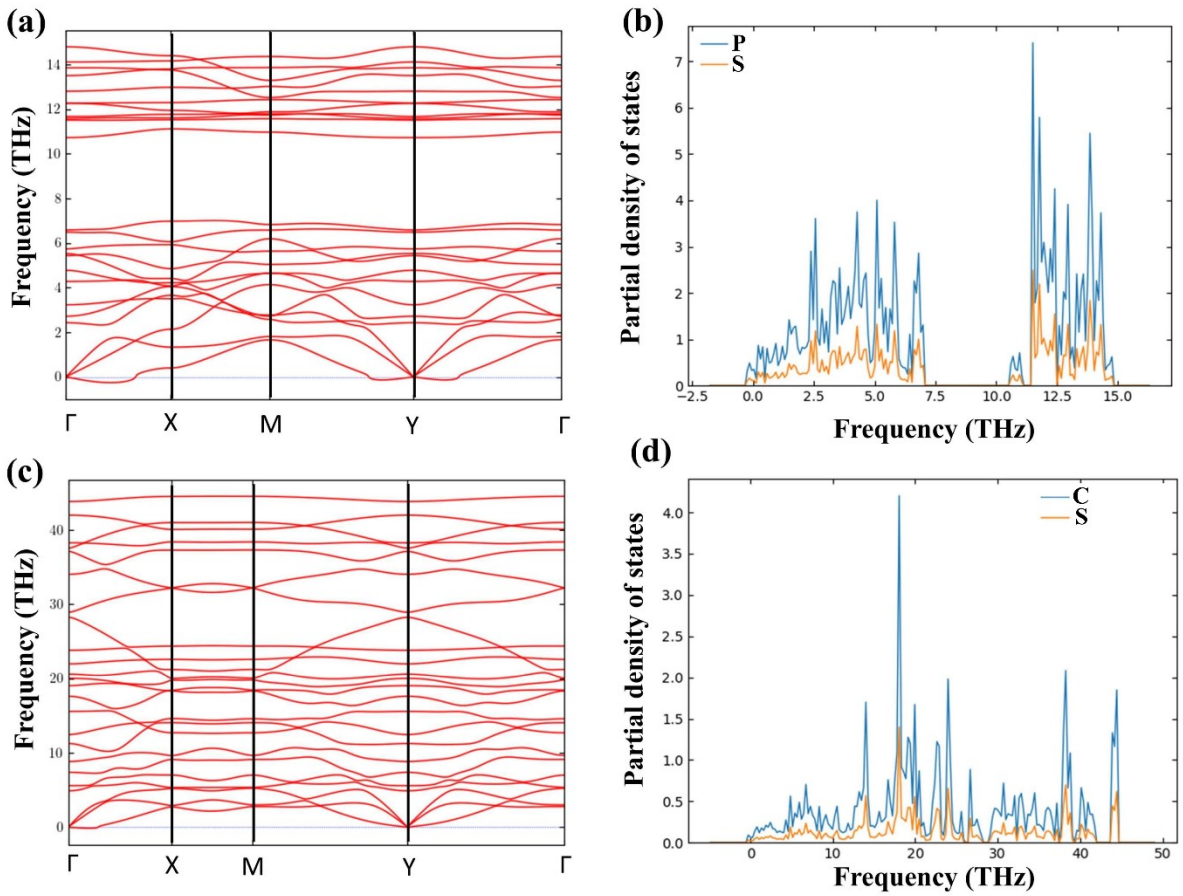

Figure S4. Phonon band structure and partial density of states for (3×3×1) pristine P_3S (a,b) and C_3S (c,d) monolayers, respectively.

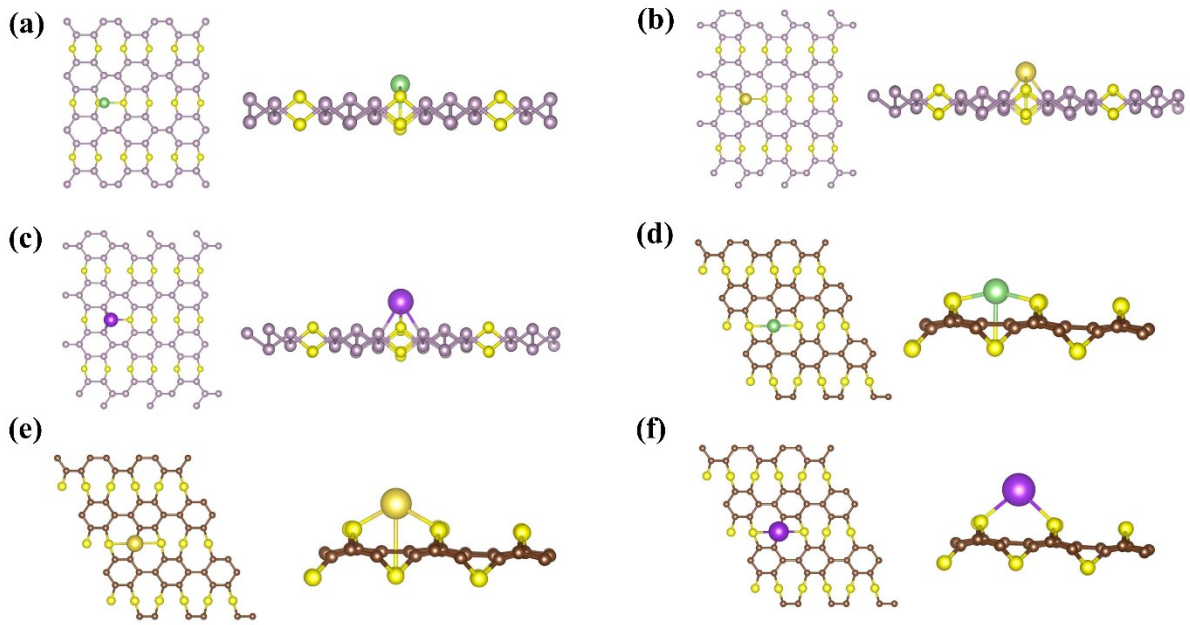

Figure S5. Relaxed structures of the single alkali metal adsorbed P_3S and C_3S monolayers at their most favored sites: (a-c) and (d-f) Li-, Na-, and K-adsorbed P_3S and C_3S systems, respectively [top and side view] (The violet, brown, yellow, green, golden yellow and purple balls represent P, C, S, Li, Na, and K atoms, respectively).

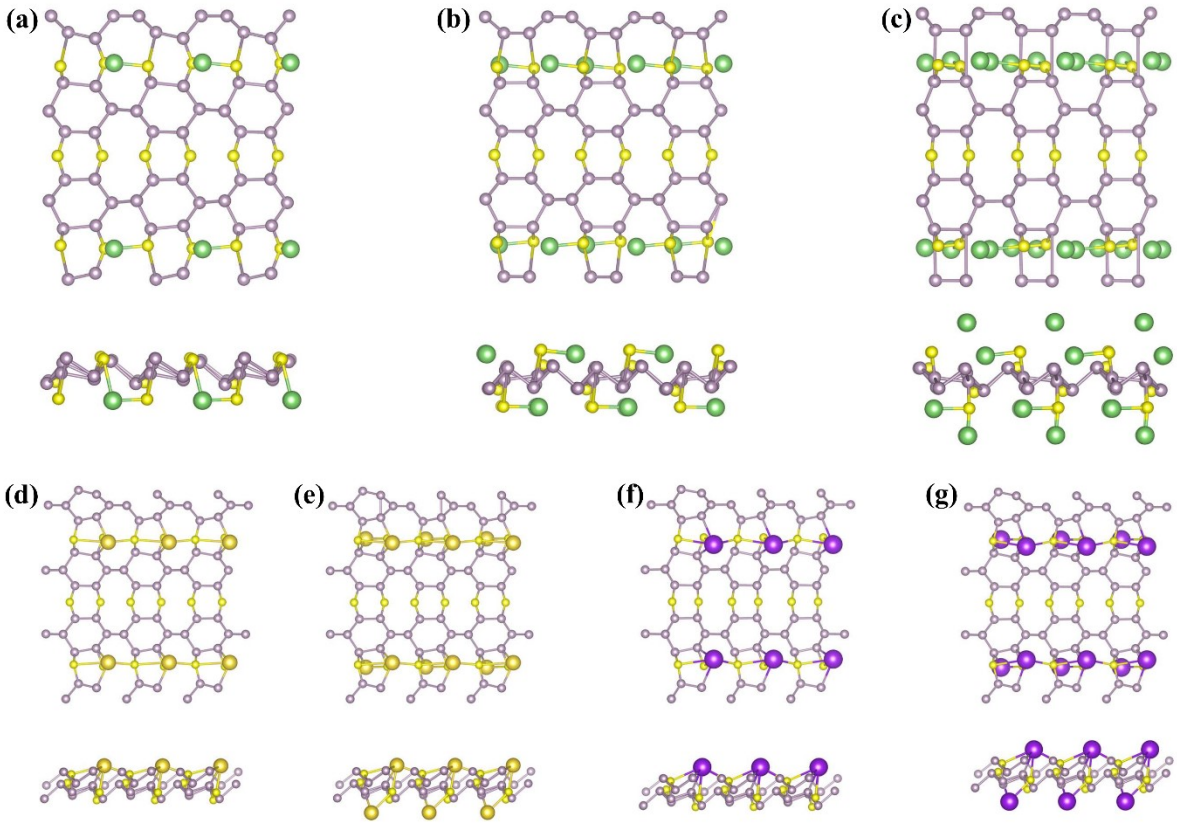

Figure S6. Optimized geometries of the (a) monolayer Li-adsorbed P_3S, (b) bilayer Li-adsorbed P_3S, (c) tetralayer Li-adsorbed P_3S, (d) monolayer Na-adsorbed P_3S, (e) bilayer Na-adsorbed P_3S, (f) monolayer K-adsorbed P_3S, and (g) bilayer K-adsorbed P_3S composite systems [top and side view] (The violet, yellow, green, golden yellow, and purple balls represent P, S, Li, Na, and K atoms, respectively).

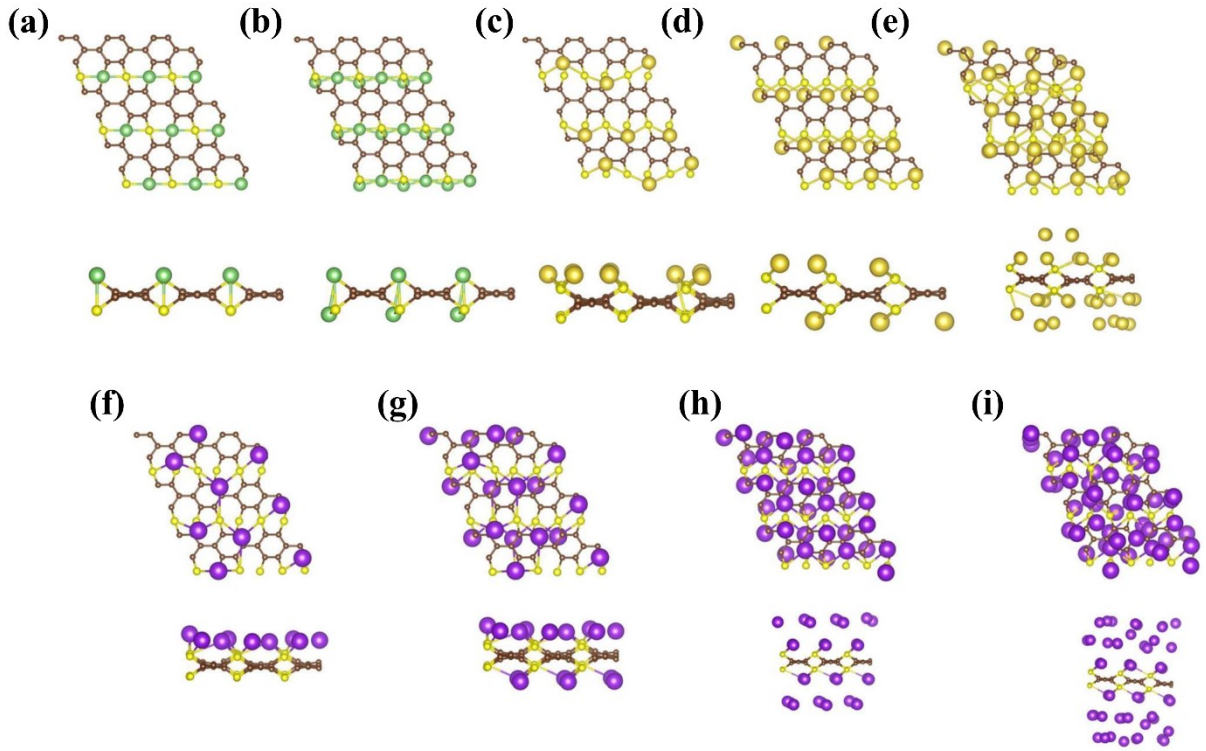

Figure S7. Optimized geometries of the (a) monolayer Li-adsorbed C_3S, (b) bilayer Li-adsorbed C_3S, (c) monolayer Na-adsorbed C_3S, (d) bilayer Na-adsorbed C_3S, (e) tetralayer Na-adsorbed C_3S, (f) monolayer K-adsorbed C_3S, (g) bilayer K-adsorbed C_3S, (h) tetralayer K-adsorbed C_3S, and (g) hexalayer K-adsorbed C_3S composite systems [top and side view] (The brown, yellow, green, golden yellow and purple balls represent C, S, Li, Na, and K atoms, respectively).

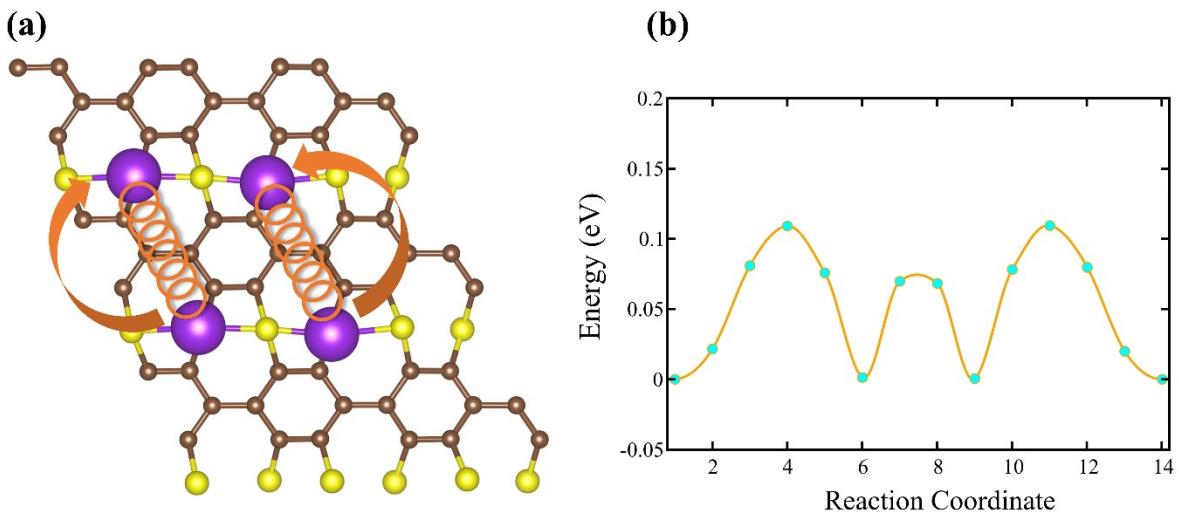

Figure S8. (a) Possible diffusion pathway of two K-atoms from one most favored T_{BH}-site to another T_{BH}-site simultaneously in C_3S monolayer and (b) its corresponding energy profile diagram.

Table S1. Structural information of pristine P_3S and C_3S monolayers.

Monolayer	**Crystal Structure (Space Group)**	**Lattice Parameters (Å, °)**	**Bond Lengths (Å)**
P_3S	Monoclinic (P2/m)	a = 6.04 b = 6.41 α = 91.63 β = 90.04 γ = 89.92	P-P: 2.26 2.27 2.28 P-S: 2.16
C_3S	Triclinic (P1)	a = 4.44 b = 5.63 α = 90.23 β = 90.92 γ = 113.23	C-C: 1.44 C-S: 1.78

Table S2. Adsorption energies (E_{ad}) for the single alkali metal adsorbed P_3S and C_3S monolayers.

Monolayer	**Alkali Metal Atom**	**Adsorption Energy (E_{ad}) (eV)**	**Most Favored Site**
P_3S	Li	$T_{P\text{-}S}$: −5.48, $T_{P\text{-}P}$: −5.50, T_P: −5.28, T_S: −5.41, T_{hP}: −5.28, T_{hPS}: −5.49, and T_{BH}: −5.52,	T_{BH}
	Na	$T_{P\text{-}S}$: −5.52, $T_{P\text{-}P}$: −5.59, T_P: −5.51, T_S: −5.46, T_{hP}: −5.53, T_{hPS}: −5.55, and T_{BH}: −5.62	T_{BH}
	K	$T_{P\text{-}S}$: −6.16, $T_{P\text{-}P}$: −6.10, T_P: −6.08, T_S: −6.06, T_{hP}: −6.10, T_{hPS}: −6.11, and T_{BH}: −6.18	T_{BH}
C_3S	Li	$T_{C\text{-}S}$: −4.96, $T_{C\text{-}C}$: −4.82, T_C: −4.89, T_S: −5.02, T_h: −4.88, T_{BH}: −4.94	T_S
	Na	$T_{C\text{-}S}$: −4.60, $T_{C\text{-}C}$: −4.53, T_C: −4.65, T_S: −4.90, T_h: −4.48, T_{BH}: −4.76	T_S
	K	$T_{C\text{-}S}$: −5.27, $T_{C\text{-}C}$: −5.19, T_C: −5.17, T_S: −5.35, T_h: −5.29, T_{BH}: −5.30	T_S

Table S3. Charge transfer (Bader charge analysis) from the alkali metals to the monolayers and diffusion barrier of the different pathways for the single alkali metal adsorbed P_3S and C_3S systems.

Monolayer	**Alkali Metal Atom**	**Charge Transfer (Bader Charge Analysis) (e)**	**Diffusion Barrier (eV)**		
			Path 1 (Green)	**Path 2 (Blue)**	**Path 3 (Red)**
P_3S	Li	0.86	0.74	0.76	0.77
	Na	0.84	0.26	0.38	0.40
	K	0.87	0.57	1.12	1.27
C_3S	Li	0.86	0.68	0.75	-
	Na	0.84	0.30	0.74	-
	K	0.88	0.06	0.08	-

Table S4. Layer-by-layer adsorption energies (E_{ad}), average open-circuit voltage (OCV), and maximum theoretical capacities (C) of the alkali metal adsorbed P_3S and C_3S systems.

Monolayer	**Alkali Metal Atom**	**Layer-by-layer adsorption energies (E_{ad}) (eV)**	**Average Open-Circuit Voltage (OCV) (V)**	**Maximum Theoretical Capacities (C) (mAh/g)**
P_3S	Li	Monolayer: −2.07 Bilayer: −1.30 Trilayer: −1.26 Tetralayer: −0.88	1.38	285.97
	Na	Monolayer: −1.90 Bilayer: −1.70	1.80	142.98
	K	Monolayer: −2.28 Bilayer: −2.26	2.27	142.98
C_3S	Li	Monolayer: −1.14 Bilayer: −0.83	0.99	394.26
	Na	Monolayer: −0.89 Bilayer: −0.31 Trilayer: −0.20 Tetralayer: −0.08	0.37	788.53
	K	Monolayer: −1.16 Bilayer: −0.85 Trilayer: −0.30 Tetralayer: −0.28 Pentalayer: −0.16 Hexalayer: −0.09	0.48	1182.79

Table S5. Details of volume expansion calculation of alkali metal adsorbed P_3S and C_3S systems at their maximum adsorbed geometries.

Monolayer	**Alkali Metal Atom**	**Maximum Adsorbed Geometry**	**Old Volume (Å^3)**	**New Volume (Å^3)**	**Volume expansion (%)**
P_3S	Li	Tetralayer	6976.424	7235.892	0.037
	Na	Bilayer	6976.424	9281.76	0.33
	K	Bilayer	6976.424	9842.94	0.41
C_3S	Li	Bilayer	4510.872	4624.48	0.025
	Na	Tetralayer	4510.872	4530.288	0.004
	K	Hexalayer	4510.872	4537.937	0.006