Electronic Supplementary Material (ESI) for Nanoscale Advances.

Electronic Supporting Information

Monolayer *H*-MoS_2 with High Ion Mobility as A Promising Anode for Rubidium (Cesium)-Ion Batteries

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Table S1. The diffusion barrier (eV) and diffusion constant (T=300 K) of MX_2 and graphene for Rb and Cs.

Monolayer	Rb				Cs			
	Pathway-I		Pathway-II		Pathway-I		Pathway-II	
	Barrier	Constant	Barrier	Constant	Barrier	Constant	Barrier	Constant
H-MoS_2	0.037	2.39E-01	0.243	8.28E-05	0.036	2.48E-01	0.203	3.89E-04
H-$MoSe_2$	0.039	2.21E-01	0.237	1.04E-04	0.039	2.21E-01	0.196	5.10E-04
H-$MoTe_2$	0.042	1.97E-01	0.175	1.15E-03	0.042	1.97E-01	0.134	5.61E-03
H-WS_2	0.052	1.34E-01	0.253	5.62E-05	0.050	1.45E-01	0.221	1.94E-04
H-WSe_2	0.052	1.34E-01	0.241	8.94E-05	0.051	1.39E-01	0.222	1.86E-04
H-WTe_2	0.054	1.24E-01	0.239	9.66E-05	0.055	1.19E-01	0.211	2.85E-04
T'- MoS_2	0.122	8.92E-03	0.450	2.76E-08	0.091	2.96E-02	0.411	1.25E-07
Graphene	0.043	1.90E-01	0.048	1.56E-01	0.033	2.79E-01	0.037	2.39E-01

Table S2. Structural information obtained by PBE-D3 functional for graphene and monolayer MX_2 (M=Mo, W; X=S, Se and Te) systems. The Lattice Constants a, b and h (height).

Monolayer	a (b)/Å	h/Å
H-MoS_2	3.167	3.134
H-$MoSe_2$	3.310	3.339
H-$MoTe_2$	3.479	3.655
H-WS_2	3.185	3.134
H-WSe_2	3.331	3.336
H-WTe_2	3.558	3.606
T(*T'*)-MoS_2	3.209	3.141
Graphene	2.468	/

Table S3. The binding energy (eV) of M-top, X-top and hollow sites of MX_2 to Rb and Cs.

MX_2	Rb@MX_2			Cs@MX_2		
	M-top	X-top	Hollow	M-top	X-top	Hollow
H-MoS_2	-0.96	-0.72	-0.94	-1.17	-0.97	-1.14
H-$MoSe_2$	-0.72	-0.46	-0.67	-0.94	-0.74	-0.9
H-$MoTe_2$	-0.52	-0.33	-0.48	-0.74	-0.6	-0.7
H-WS_2	-0.64	-0.39	-0.59	-0.85	-0.64	-0.81
H-WSe_2	-0.47	-0.23	-0.42	-0.68	-0.47	-0.64
H-WTe_2	-0.53	-0.29	-0.48	-0.74	-0.53	-0.69
T'- MoS_2	-2.49	-2.60	-3.29	-2.53	-2.85	-2.95

Table S4. The Rb and Cs ion charges (e) were calculated by Bader charge scheme. The diffusion energy barrier (eV) from pathway-I of *H*-MX_2 and graphene for Rb and Cs. The e_S represents the charge on stable site. The e_T represents the charge on transition site. The Δe_d represents the charge difference between e_T and e_S ($\Delta e_d = e_T - e_S$).

H-MX_2	Rb@*H*-MX_2				Cs@*H*-MX_2			
	Barrier	e_S	e_T	Δe_d	Barrier	e_S	e_T	Δe_d
H-MoS_2	0.037	0.8788	0.8819	0.0031	0.036	0.8767	0.8810	0.0043
H-$MoSe_2$	0.039	0.8549	0.8597	0.0048	0.039	0.8557	0.8618	0.0061
H-$MoTe_2$	0.042	0.8292	0.8368	0.0076	0.042	0.8259	0.8349	0.0090
H-WS_2	0.052	0.8748	0.8796	0.0048	0.050	0.8757	0.8851	0.0094
H-WSe_2	0.052	0.8542	0.8597	0.0055	0.051	0.8535	0.8649	0.0114
H-WTe_2	0.054	0.8359	0.8452	0.0093	0.055	0.8273	0.8417	0.0144

Table S5. The average binding energy (eV) of different layers of adsorption Rb on *H*-MX_2 and graphene. The corresponding storage density (atom/$Å^2$), theoretical capacity (mAh/g) and open circuit voltage (V) of the optimal adsorption system. The * indicating the amount of Rb adsorption.

Materials	E_b (*Rb@M_9X_{18})						Storage Density	Theoretical Capacity	OCV
	@1L (*=4)	@2L (*=8)	@3L (*=12)	@4L (*=16)	@5L (*=20)	@6L (*=24)			
H-MoS_2	-0.48	-0.24	-0.10	-0.10	-0.03	~~0.07~~	0.23	372.05	0.96
H-$MoSe_2$	-0.41	-0.18	-0.07	-0.01	~~0.05~~	/	0.18	187.72	0.72
H-$MoTe_2$	-0.48	-0.27	~~0.05~~	/	/	/	0.08	67.84	0.52
H-WS_2	-0.38	-0.15	~~0.01~~	/	/	/	0.10	96.08	0.64
H-WSe_2	-0.34	-0.10	~~0.02~~	/	/	/	0.09	69.72	0.47
H-WTe_2	-0.46	-0.21	~~0.00~~	/	/	/	0.08	54.26	0.53
Materials	E_b (*Rb@C_{32})						Storage Density	Theoretical capacity	OCV
	@1L				@2L				
Graphene	*=1	*=2	*=3	*=4	*=2	*=4	0.01	69.79	0.01
	-0.01	~~0.01~~	~~0.02~~	~~0.02~~	~~0.05~~	~~0.02~~			

Table S6. The average binding energy (eV) of different layers of adsorption Cs on *H*-MX_2 and graphene. The corresponding Storage density (atom/Å^2), theoretical capacity (mAh/g) and open circuit voltage (V) of the optimal adsorption system. The * indicating the amount of Cs adsorption.

Materials	E_b (*Cs@M_9X_{18})				Storage Density	Theoretical Capacity	OCV
	@1L (*=4)	@2L (*=8)	@3L (*=12)	@4L (*=16)			
H-MoS_2	-0.43	-0.20	-0.07	~~0.00~~	0.14	223.23	1.17
H-$MoSe_2$	-0.40	-0.16	-0.08	~~0.01~~	0.13	140.79	0.94
H-$MoTe_2$	-0.38	-0.18	~~0.01~~	/	0.08	67.84	0.74
H-WS_2	-0.32	-0.10	~~0.01~~	/	0.10	96.08	0.85
H-WSe_2	-0.28	-0.08	~~0.04~~	/	0.09	69.72	0.68
H-WTe_2	-0.58	-0.28	~~0.00~~	/	0.08	54.26	0.74
Materials	E_b (*Cs@C_{32})				Storage Density	Theoretical Capacity	OCV
	@1L			@2L			
Graphene	*=1	*=2	*=3	*=2	0.02	139.59	0.19
	-0.19	-0.05	~~0.02~~	~~0.03~~			

Table S7. The charge (e) of *Rb@*H*-MoS_2 and *Cs@*H*-MoS_2 obtained from Bader charge transfer. The (+) and (-) numbers indicate the positive charge (lost electrons) and the negative charge (get electrons) on each layer of *Rb@*H*-MoS_2 and *Cs@*H*-MoS_2, respectively. And the (-) bold number indicates the negative charge (get electrons) carried on the *H*-MoS_2 of *Rb@*H*-MoS_2 and *Cs@*H*-MoS_2. The structure and layer naming can be seen in Figure 2a in the main text. The * indicating the amount of Rb/Cs adsorption.

System	*Rb@*H*-MoS_2					*Cs@*H*-MoS_2		
	*=4	*=8	*=12	*=16	*=20	*=4	*=8	*=12
	@1L	@2L	@3L	@4L	@5L	@1L	@2L	@3L
Up-L3					+0.199			
Up-L2			+0.096	+0.084	-0.242			+0.150
Up-L1	+1.366	+1.433	+1.389	+1.406	+1.520	+1.399	+1.456	+1.261
MoS_2	**-1.366**	**-2.868**	**-3.106**	**-2.981**	**-2.957**	**-1.399**	**-2.906**	**-2.792**
Down-L1		+1.435	+1.621	+1.413	+1.388		+1.450	+1.380
Down-L2				+0.078	+0.092			

Table S8. The lattice constant *a*, *b* and *h* (Å), volume of *H*-MoS_2 (Å^3), change rate (%) and theoretical capacitance (mAh/g) of pure *H*-MoS_2 monolayer, *Rb@*H*-MoS_2 and *Cs@*H*-MoS_2. The * indicating the amount of Rb/Cs adsorption.

*Rb(Cs)@*H*-MoS_2	Lattice Constant *a* (*b*)	Lattice Constant Change Rate	*h* (*H*-MoS_2)	Volume (*H*-MoS_2)	Volume Change Rate	Theoretical Capacitance
Pure-MoS_2	9.50	/	3.13	244.95	/	/
1 Rb	9.63	1.37%	3.11	249.77	1.97%	18.60
4 Rb	9.64	1.47%	3.11	250.29	2.18%	74.41
8 Rb	9.67	1.79%	3.14	253.88	3.64%	148.42
12 Rb	9.95	4.74%	2.99	256.36	4.66%	223.23
16 Rb	9.95	4.74%	2.99	257.22	4.66%	297.64
20 Rb	9.94	4.63%	3.00	253.96	4.80%	372.05
1 Cs	9.63	1.37%	3.11	249.61	1.90%	18.60
4 Cs	9.67	1.79%	3.10	250.80	2.39%	74.41
8 Cs	9.74	2.53%	3.11	255.10	4.14%	148.42
12 Cs	9.95	4.74%	3.01	254.22	5.36%	223.23

Table S9. The binding energy (eV) of C-top, C-bright and Hollow sites of graphene to Li, Rb and Cs.

Alkali@Graphene	C-top	C-bridge	Hollow
Li	0.11	0.11	-0.19
Rb	0.05	0.05	-0.01
Cs	-0.14	-0.15	-0.19

Table S10. The lattice constant *a*, *b* and *h* (Å), volume of *H*-MX_2 (Å^3) and volume change rate (%)of pure MX_2 monolayer, *Rb@ MoS_2 and *Cs@ MoS_2. The * indicating the amount of Rb/Cs adsorption.

Systems		Pure-MX_2	*Rb@MX_2					*Cs@MX_2			
			*=1	*=4	*=8	*=12	*=16	*=1	*=4	*=8	*=12
$MoSe_2$	*a* (*b*)	9.93	10.01	10.01	10.04	10.28	10.27	10.02	10.05	10.11	10.14
	h	3.34	3.33	3.34	3.29	3.37	3.37	3.32	3.32	3.33	3.35
	V	285.21	288.96	289.82	287.20	308.41	307.81	288.66	290.39	294.76	298.29
	Change rate	/	1.31%	1.62%	0.70%	8.14%	7.93%	1.21%	1.82%	3.35%	4.59%
$MoTe_2$	*a* (*b*)	10.44	10.73	10.73	10.89	/	/	10.73	10.75	10.90	/
	h	3.66	3.58	3.58	3.77	/	/	3.58	3.58	3.78	/
	V	345.46	356.94	356.94	387.18	/	/	356.94	358.28	388.92	/
	Change rate	/	3.32%	3.32%	12.08%	/	/	3.32%	3.71%	12.58%	/
WS_2	*a* (*b*)	9.56	9.61	9.59	9.58	/	/	9.62	9.64	9.67	/
	h	3.13	3.12	3.12	3.13	/	/	3.12	3.10	3.16	/
	V	247.73	249.53	248.49	248.77	/	/	250.05	249.48	255.89	/
	Change rate	/	0.73%	0.31%	0.42%	/	/	0.94%	0.71%	3.30%	/
WSe_2	*a* (*b*)	9.99	10.00	9.97	9.97	/	/	10.00	10.01	10.03	/
	h	3.34	3.35	3.35	3.35	/	/	3.35	3.35	3.32	/
	V	288.67	290.11	288.37	288.37	/	/	290.11	290.69	289.24	/
	Change rate	/	0.50%	-0.10%	-0.10%	/	/	0.50%	0.70%	0.20%	/
WTe_2	*a* (*b*)	10.67	10.76	10.74	10.79	/	/	10.76	10.77	10.75	/
	h	3.61	3.60	3.60	4.21	/	/	3.59	3.59	4.22	/
	V	355.92	360.95	359.61	424.47	/	/	359.95	360.61	422.33	/
	Change rate	/	1.41%	1.04%	19.26%	/	/	1.13%	1.32%	18.66%	/

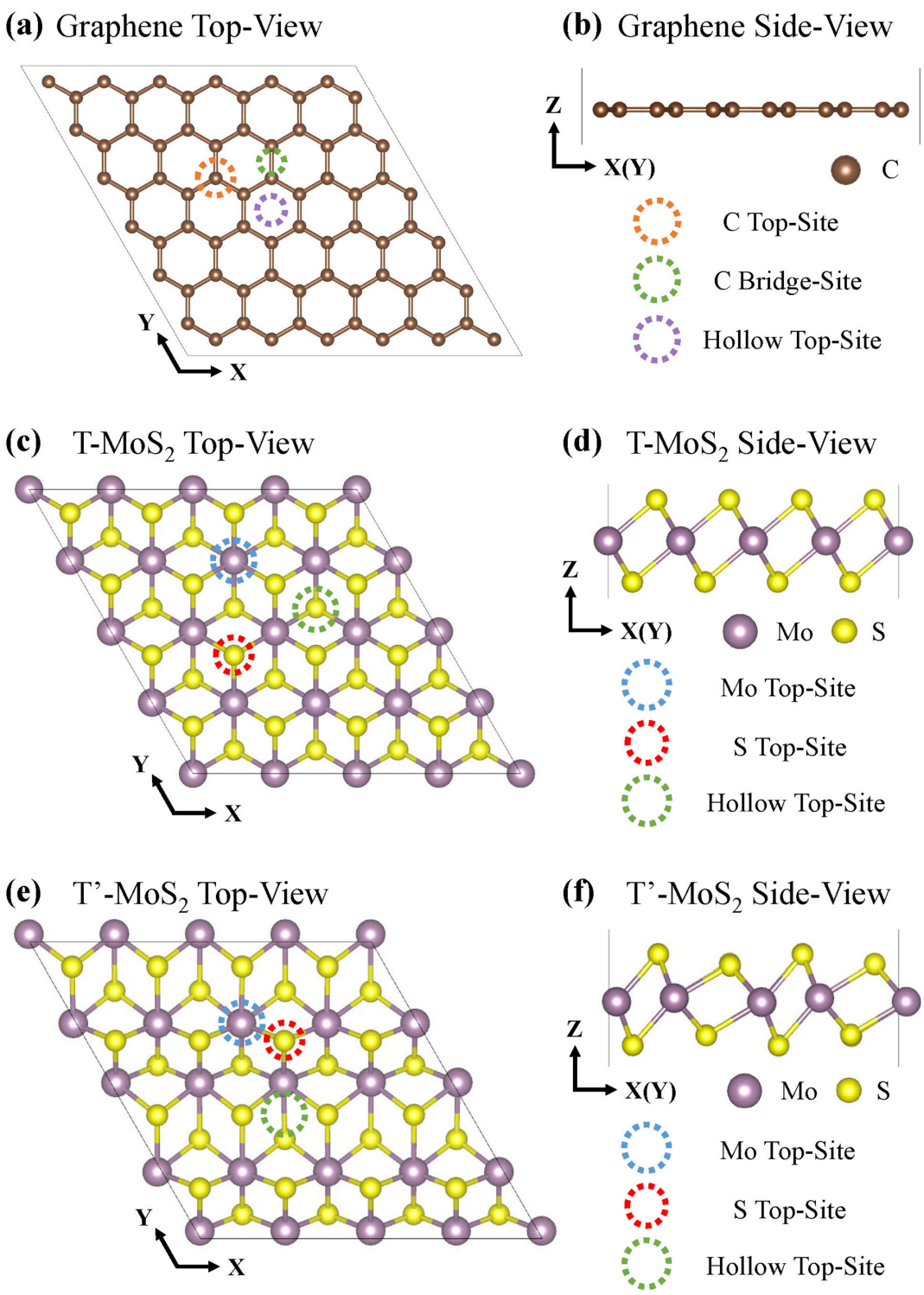

Figure S1 The (a) top and (b) side views of the atomic structure of the 6×6×1 graphene supercell. The (c) top and (d) side views of the atomic structure of the 4×4×1 monolayer *T*-MoS_2 supercell. The (e) top and (f) side views of the atomic structure of the 4×4×1 monolayer *T'*-MoS_2 supercell.

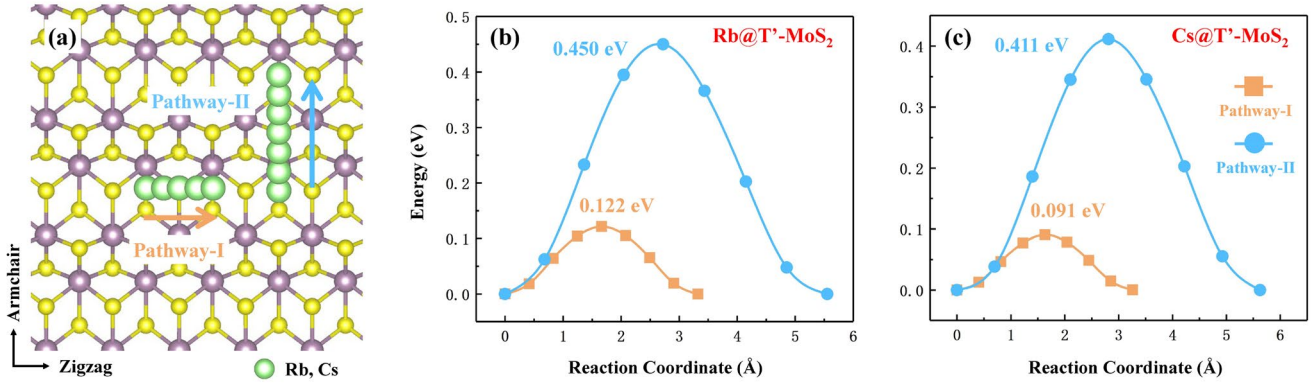

Figure S2 (a) The two universal diffusion pathways (pathway-I along zigzag and pathways-II along armchair direction) for Rb and Cs ions diffusing on *T'*-MoS_2 monolayer. Diffusion energy curves of (b) Rb and (c) Cs ions on *T'*-MoS_2 monolayer.

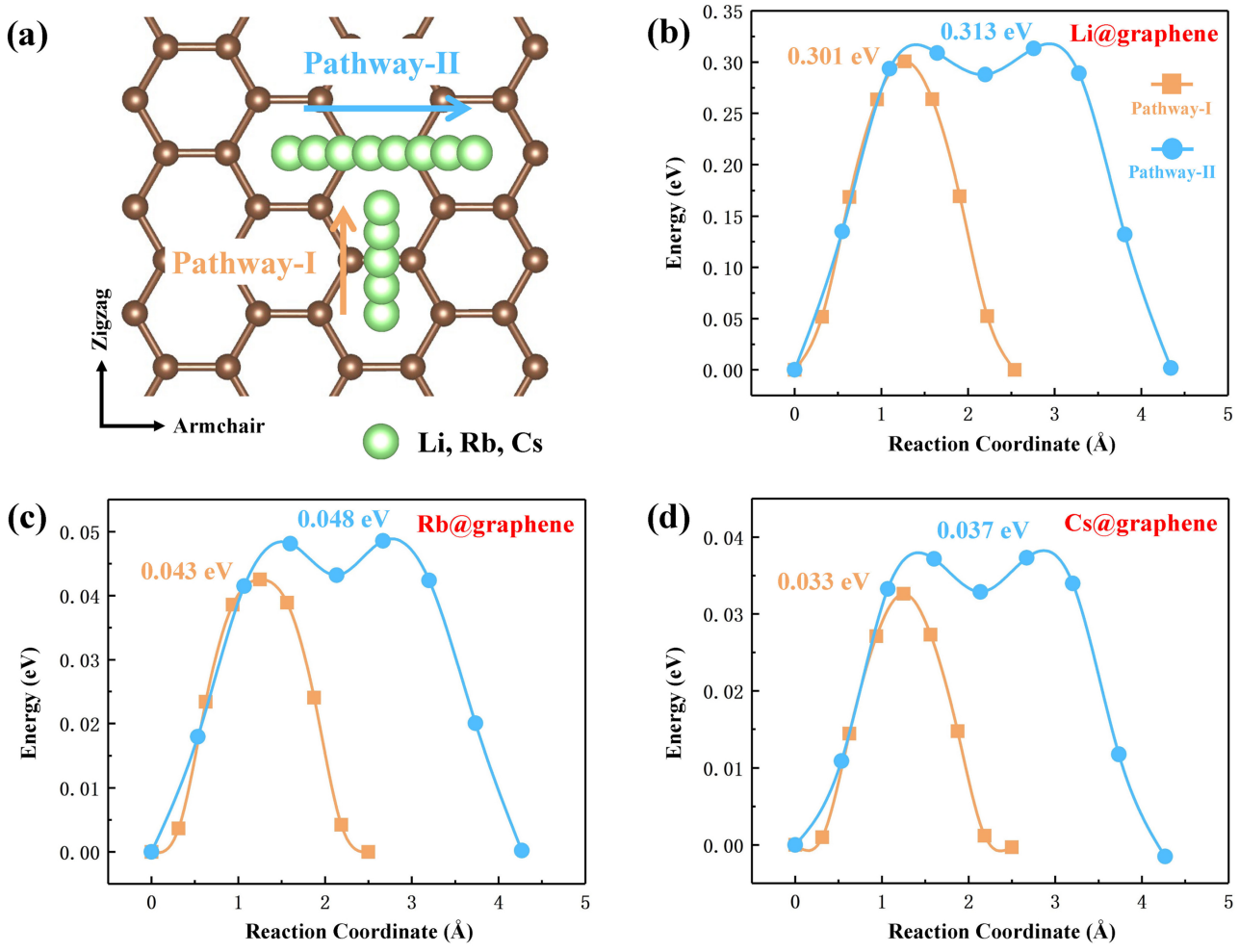

Figure S3 (a) The two universal diffusion pathways (pathway-I along zigzag and pathways-II along armchair direction) for Li, Rb and Cs ions diffusing on graphene. Diffusion energy curves of (b) Li, (c) Rb and (d) Cs ions on graphene.

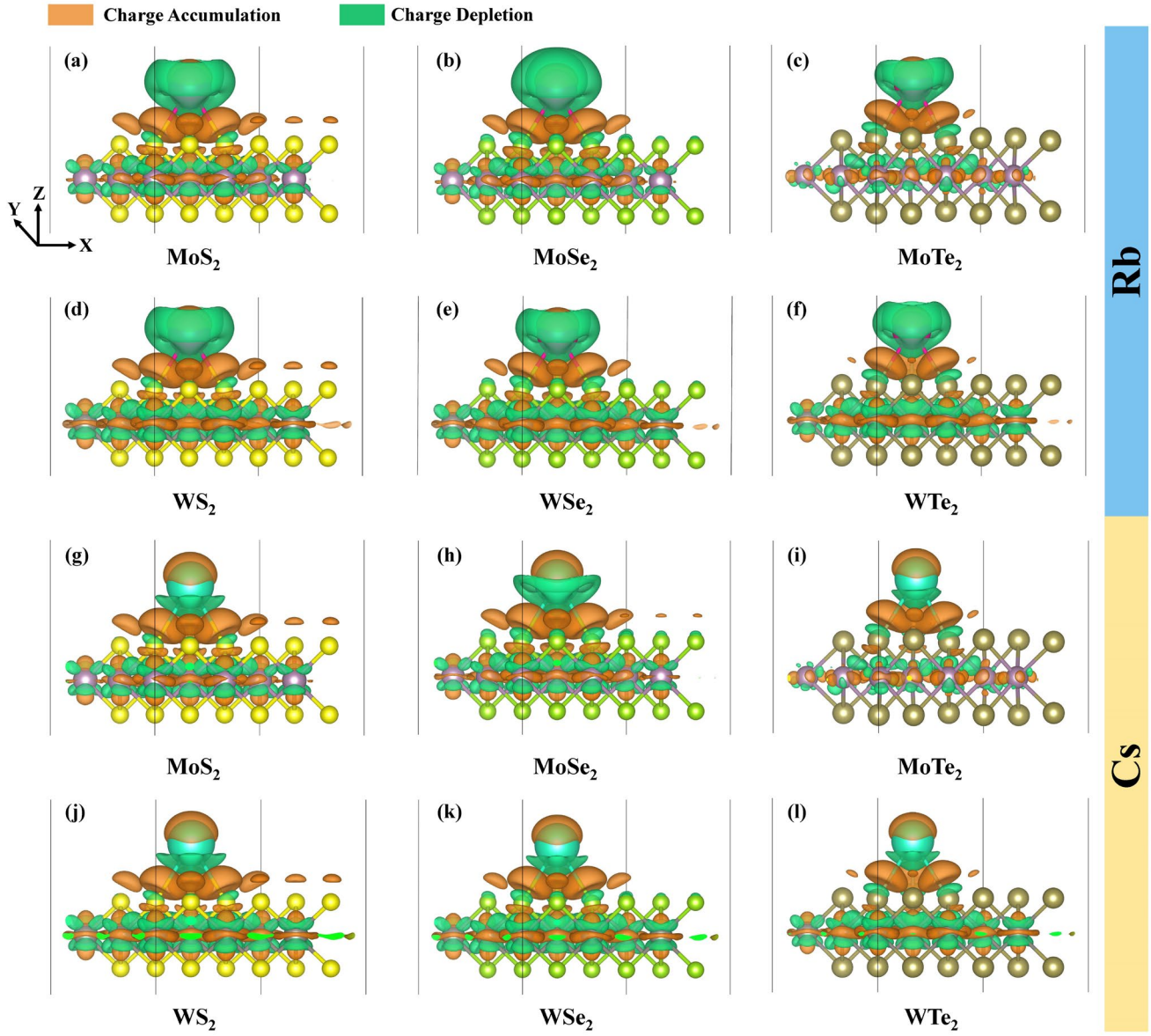

Figure S4. Difference charge density of Rb at the stable adsorption site (M-top) of monolayer (a) *H*-MoS_2, (b) *H*-$MoSe_2$, (c) *H*-$MoTe_2$, (d) *H*-WS_2, (e) *H*-WSe_2, (f) *H*-WTe_2. Difference charge density of Cs at the stable adsorption site (M-top) of monolayer (g) *H*-MoS_2, (h) *H*-$MoSe_2$, (i) *H*-$MoTe_2$, (j) *H*-WS_2, (k) *H*-WSe_2 and (l) *H*-WTe_2. Orange and green colors with the isosurface value of 0.001 e/A^3, represent charge accumulation and depletion, respectively.

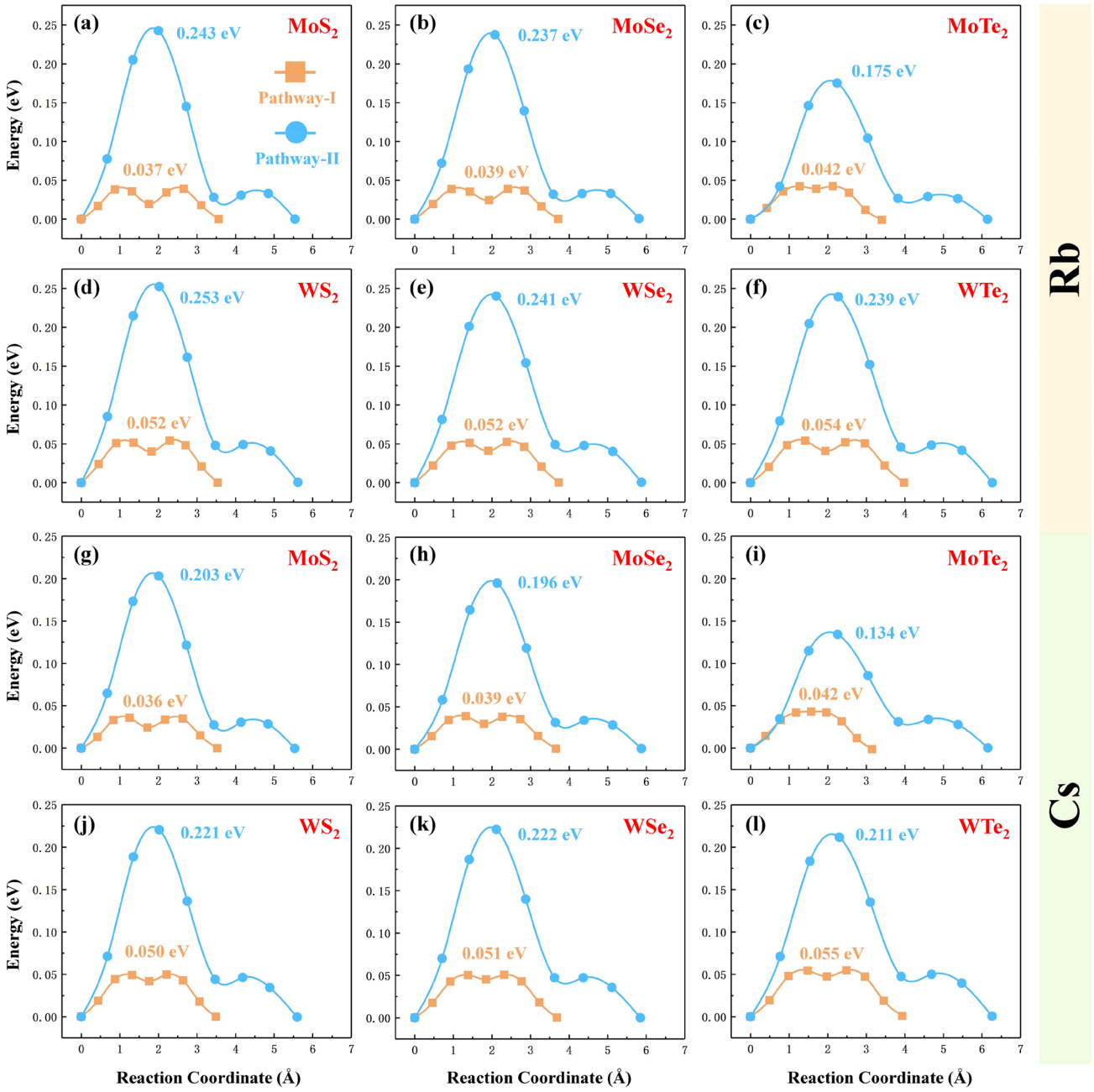

Figure S5. The diffusion energy curves of two universal pathways (pathway-I along zigzag and pathways-II along armchair direction) for (a) Rb@*H*-MoS_2, (b) Rb@*H*-$MoSe_2$, (c) Rb@*H*-$MoTe_2$, (d) Rb@*H*-WS_2, (e) Rb@*H*-WSe_2, (f) Rb@*H*-WTe_2, (g) Cs@*H*-MoS_2, (h) Cs@*H*-$MoSe_2$, (i) Cs@*H*-$MoTe_2$, (j) Cs@*H*-WS_2, (k) Cs@*H*-WSe_2 and (l) Cs@*H*-WTe_2.

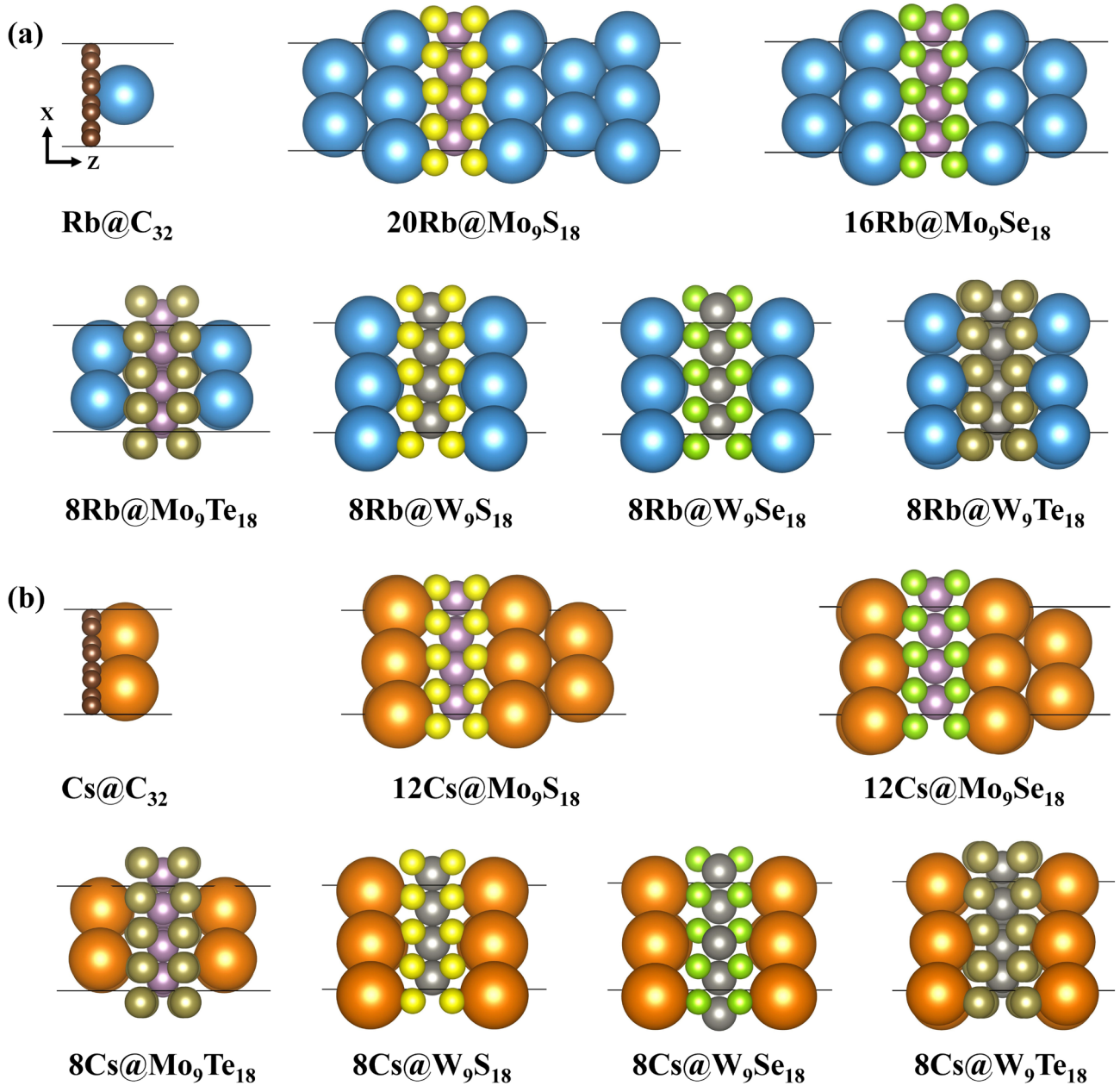

Figure S6 Schematic diagram of the maximum adsorption capacity of 3×3×1 *H*-MX_2 supercell and 4×4×1 graphene supercell for (a) Rb and (b) Cs.