Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

B_5N_3 as a potential high-capacity electrode material for calcium ion batteries

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Fig. S1

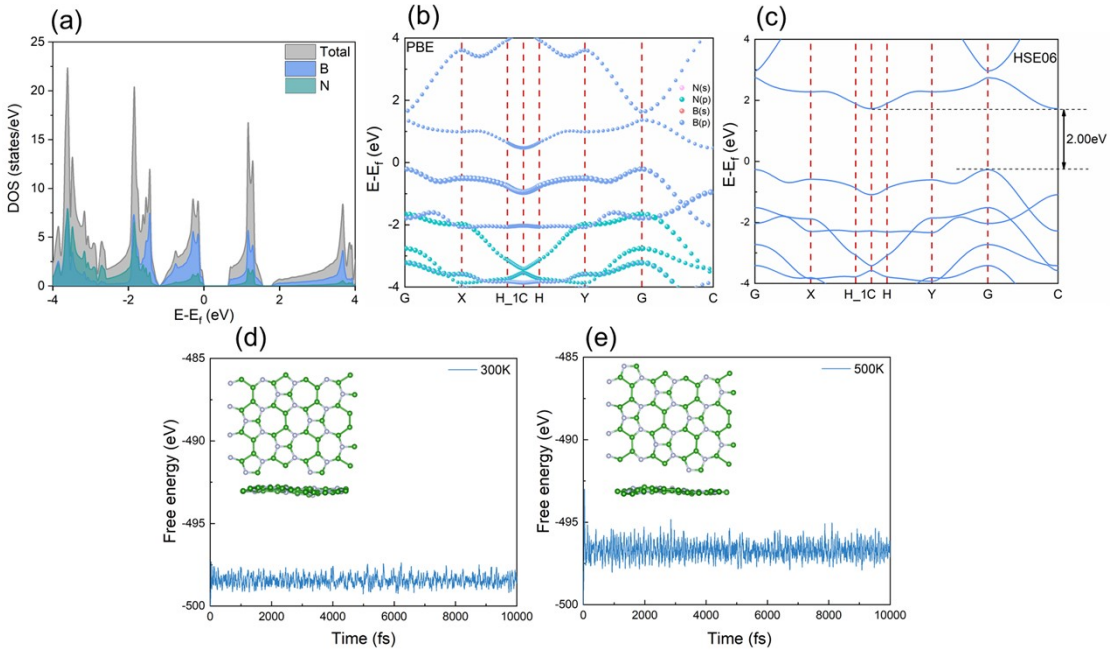

Fig. S1 Electronic property and thermal stability of B_5N_3. (a) The density of states (DOS) and band structure of B_5N_3 via the (b) PBE and (c) HSE06 functionals. The free energy of B_5N_3 for AIMD simulations over 10 ps at (d) 300K and (e) 500K.

The calculated band structure result shows that the valence band maximum (VBM) and the conduction band minimum (CBM) are located at different high symmetry point, forming an indirect band gap. The indirect band gaps of B_5N_3 are 0.67 eV and 2.00 eV in terms of the PBE and HSE06 method, respectively.

Fig. S2

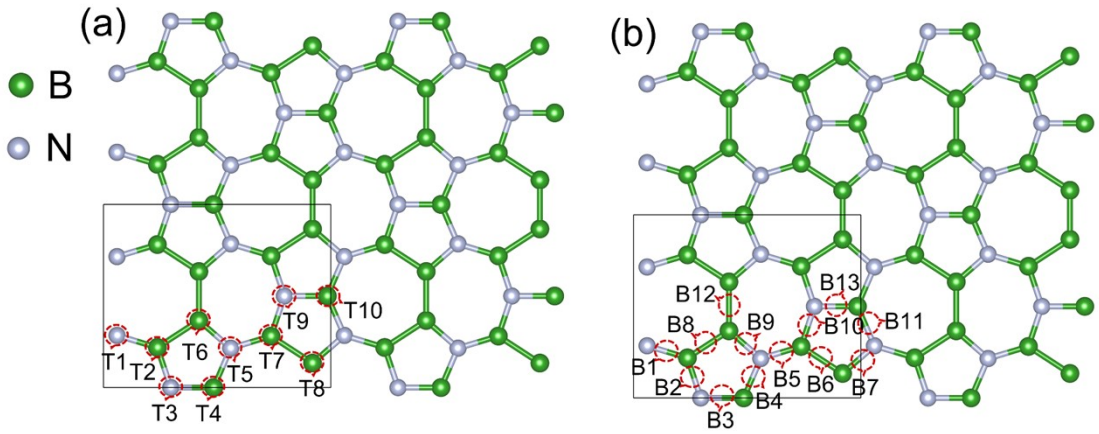

Fig. S2 The possible adsorption (a) top sites and (b) bridge sites for metal atom on B_5N_3.

Fig. S3

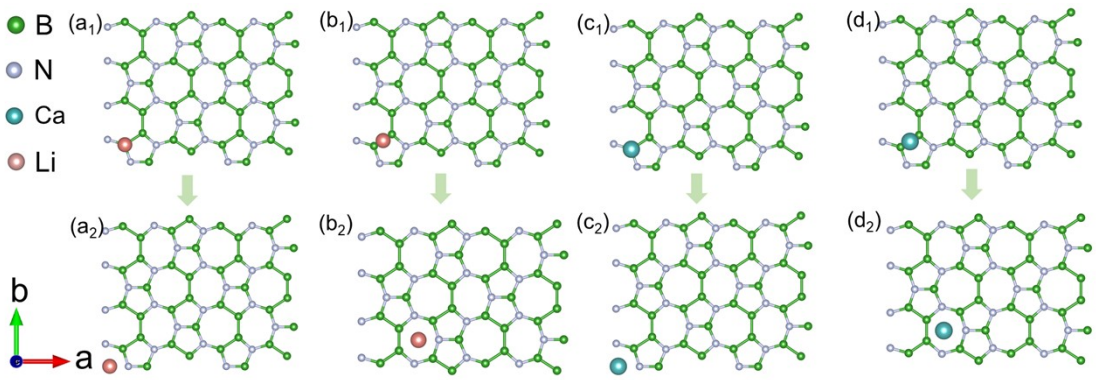

Fig. S3 The initial structure of Li system: (a_1) T2 site; (b_1) B8 site; the optimized structure of Li system: (a_2) T2 site; (b_2) B8 site; the initial structure of Ca system: (c_1) T2 site; (d_1) B8 site; the optimized structure of Ca system: (c_2) T2 site; (d_2) B8 site.

The initial and optimized structures of Li and Ca systems are shown in Fig. S3. And the corresponding adsorption energies are listed in Table S1 (Li) and Table S2 (Ca). The calculated result shows that the adsorption energies of most top and bridge sites are equal to that of hollow sites. The optimized structures also show that corresponding Ca and Li atom cannot be stably adsorbed on these top and bridge sites. Therefore, considering Li, Na and K belong to the alkali metal, which always exhibit similar adsorption behavior, we only computed the adsorption energies on all hollow sites of B_5N_3 for Na and K, as summarized in Fig. 2(b).

Fig. S4

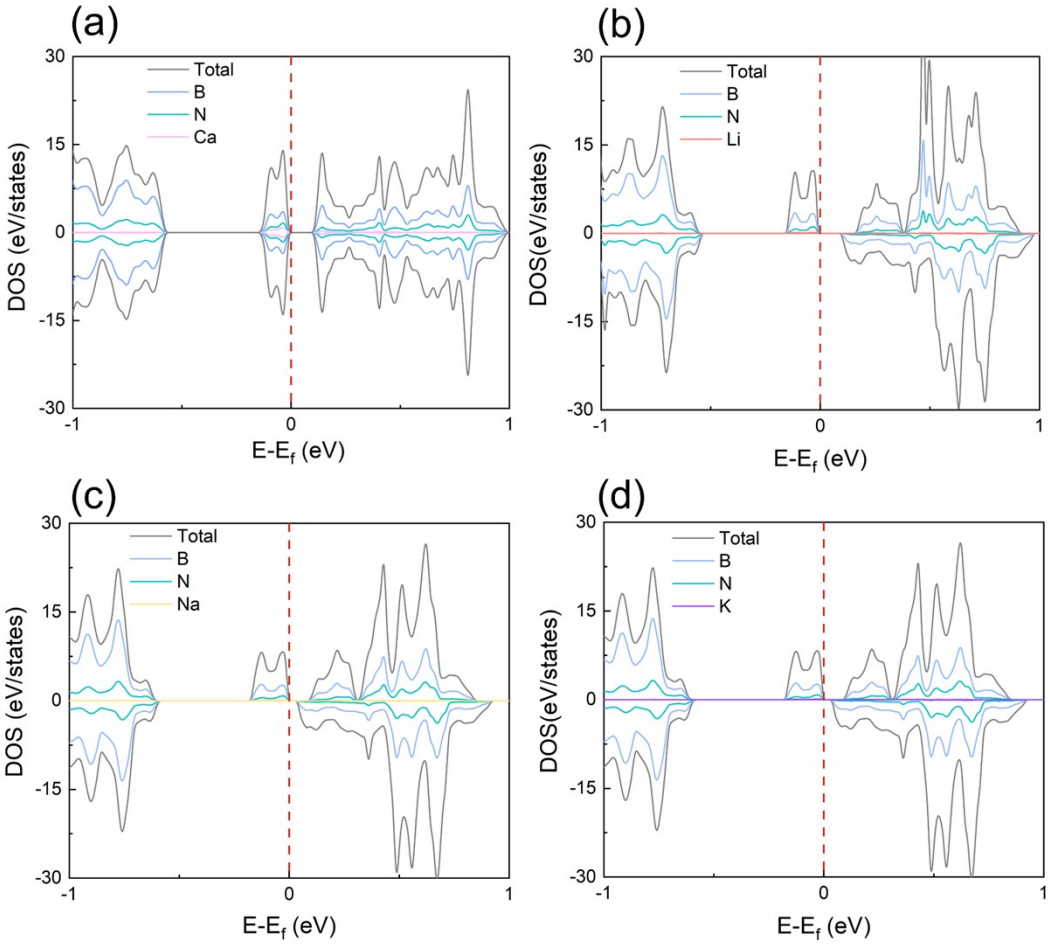

Fig. S4 The density of states (DOS) of metal-adsorbed on B_5N_3: (a) Ca, (b) Li, (c) Na and (d) K. The band gaps of Ca, Li, Na and K system are 0.11 eV, 0.09 eV, 0.03 eV and 0.02 eV, respectively.

Fig. S5

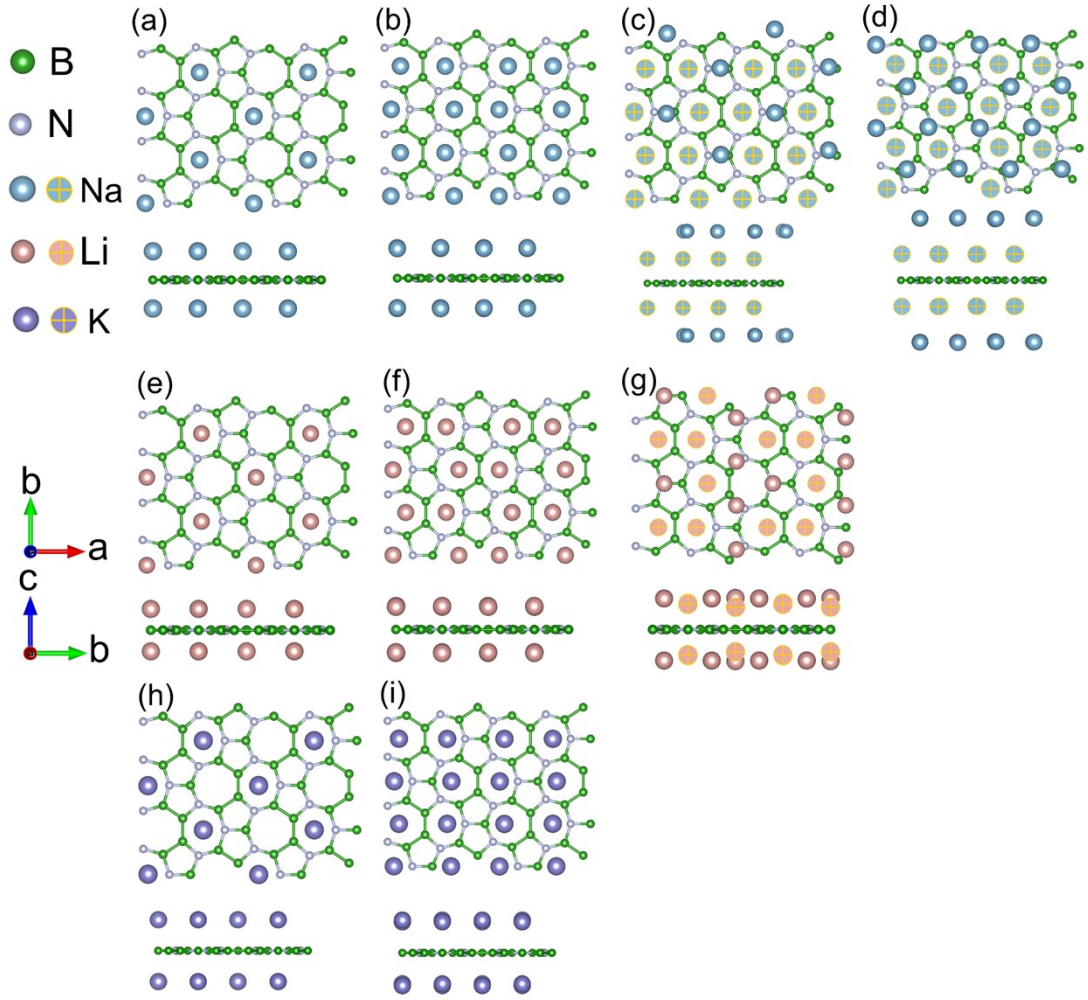

Fig. S5 The optimized structures of top view and side view of (a) $B_5N_3Na_2$, (b) $B_5N_3Na_4$, (c) $B_5N_3Na_6$, (d) $B_5N_3Na_8$, (e) $B_5N_3Li_2$, (f) $B_5N_3Li_4$, (g) $B_5N_3Li_6$, (h) $B_5N_3K_2$, (i) $B_5N_3K_4$.

Fig. S6

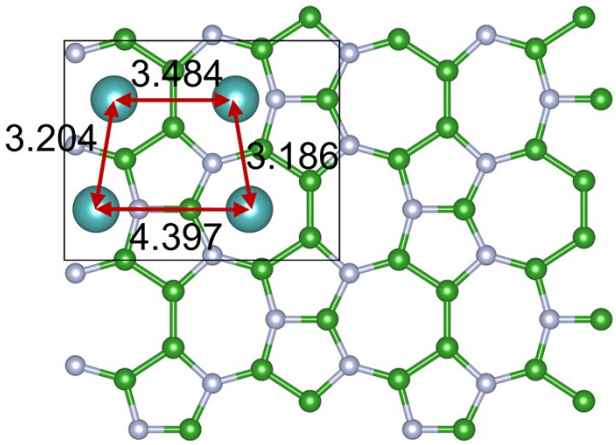

Fig. S6 The distances of the optimized H3 site and H4 site for Ca system.

We defined the distance mismatch parameter to investigate the adsorption performance of substrate. As shown in Fig. S6, the average distance (^{d_1}) is 3.57 Å for Ca system. The equilibrium distance (^{d_2}) for Ca is 3.85 Å, which is given by our previous work.[1] Therefore, the distance mismatch (^{m}) can be calculated by the following equation:

$$m = |d_1 - d_2|/d_1 \quad (1)$$

From the definition and equation, we can calculate the distance mismatches for different metal systems, and the results are 7.8 % (Ca), 18.3 % (Li), 1.1 % (Na) and 28.4 % (K).

Fig. S7

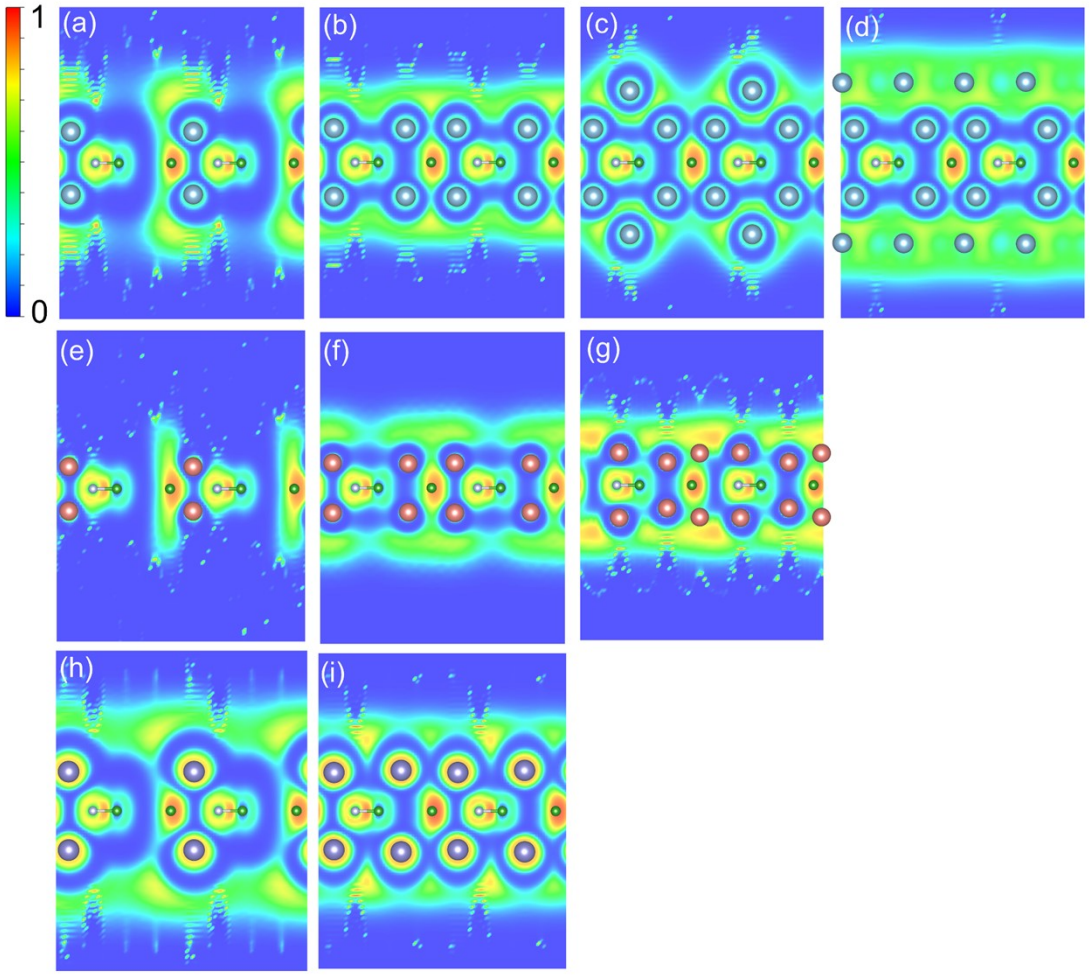

Fig. S7 The electron localization function (ELF) maps of (a) $B_5N_3Na_2$, (b) $B_5N_3Na_4$, (c) $B_5N_3Na_6$, (d) $B_5N_3Na_8$, (e) $B_5N_3Li_2$, (f) $B_5N_3Li_4$, (g) $B_5N_3Li_6$, (h) $B_5N_3K_2$, and (i) $B_5N_3K_4$.

Fig. S8

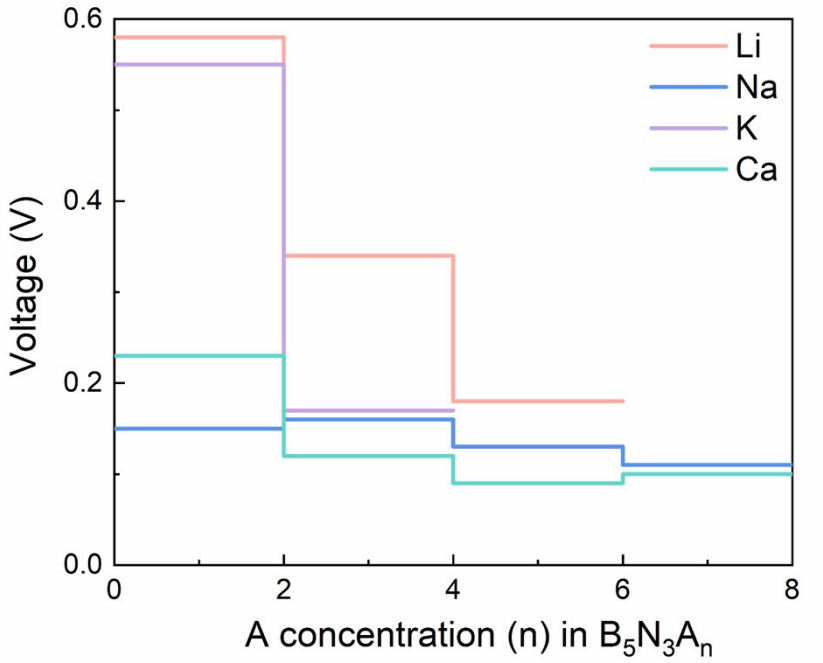

Fig. S8 The voltage profile diagram of different metal adsorption on B_5N_3.

The voltage profile diagram of different metal is shown in Fig. S8. As we can observe, the trend of OCV with the concentration of different metal is consistent with the trend of adsorption energy. The low OCV value not only prevents the formation of metal cluster but also ensures the high energy density of batteries.

Fig. S9

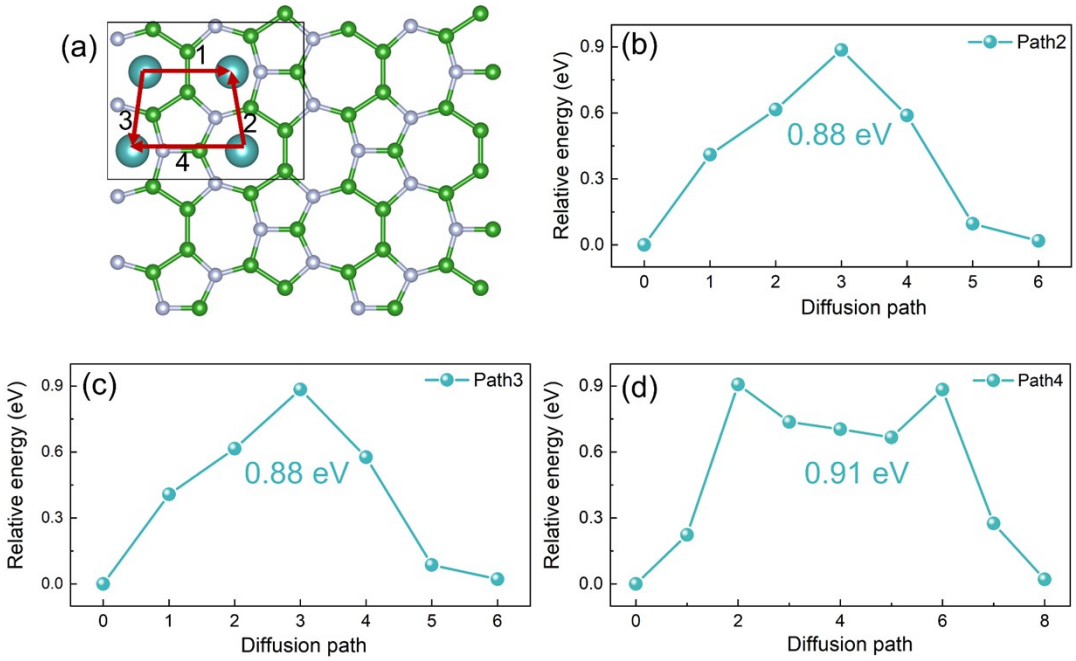

Fig. S9 (a) The schematic diagram of Ca diffusion pathways and (b) - (d) the corresponding energy barrier profiles on B_5N_3.

Fig. S10

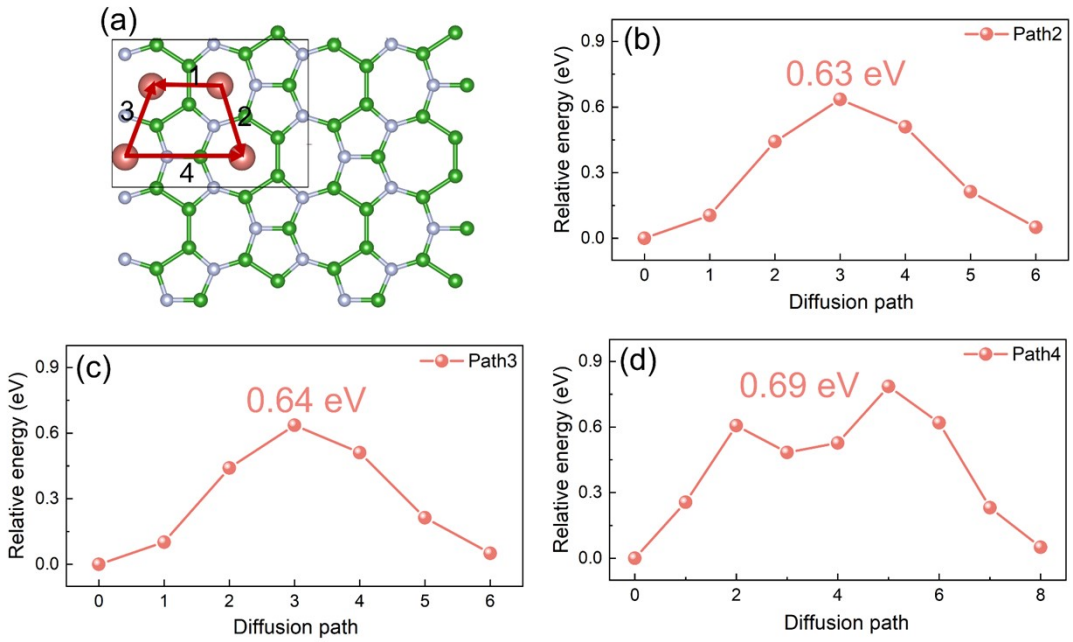

Fig. S10 (a) The schematic diagram of Li diffusion pathways and (b) - (d) the corresponding energy barrier profiles on B_5N_3.

Fig. S11

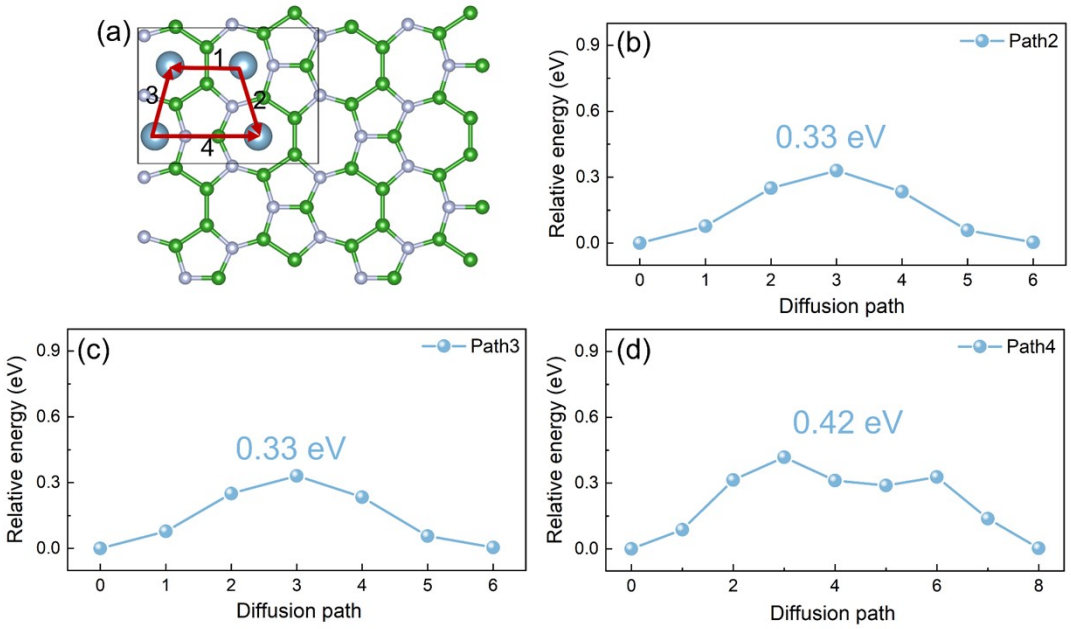

Fig. S11 (a) The schematic diagram of Na diffusion pathways and (b) - (d) the corresponding energy barrier profiles on B_5N_3.

Fig. S12

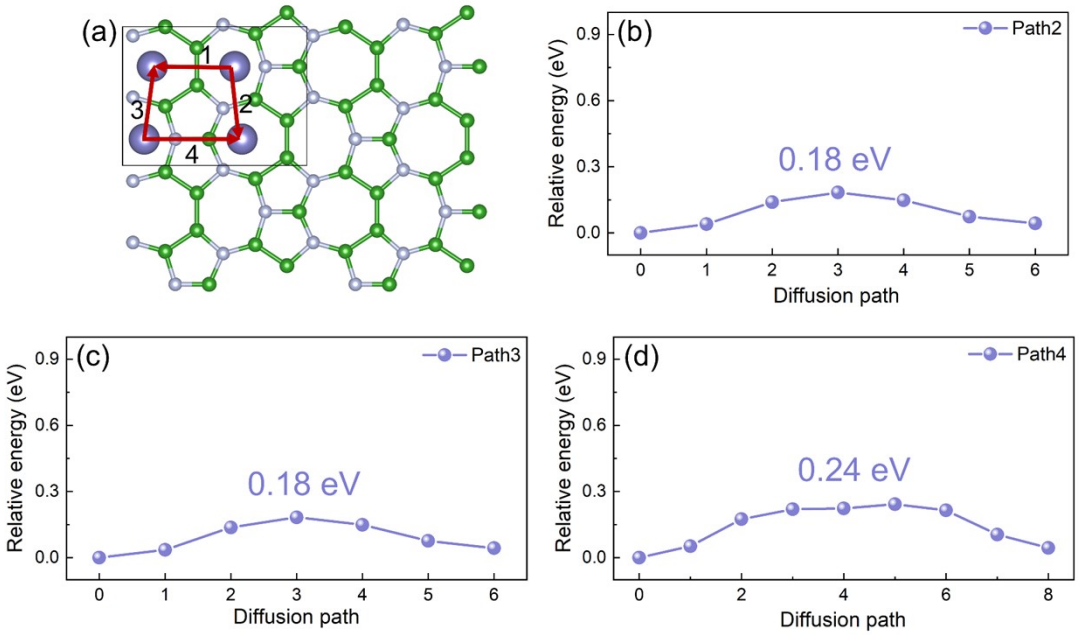

Fig. S12 (a) The schematic diagram of K diffusion pathways and (b) - (d) the corresponding energy barrier profiles on B_5N_3.

Table S1

Table S1. The calculated adsorption energy of different sites for single Li on B_5N_3

Site	E_{ads}(eV)	Site	E_{ads}(eV)
Hollow1	-0.12	Bridge1	-0.54
Hollow2	-0.12	Bridge2	-0.54
Hollow3	-0.54	Bridge3	-0.54
Hollow4	-0.48	Bridge4	-0.54
Top1	-0.54	Bridge5	-0.54
Top2	-0.54	Bridge7	-0.12
Top3	-0.54	Bridge8	-0.54
Top4	-0.48	Bridge9	-0.54
Top5	-0.54	Bridge10	-0.12
Top8	-0.54	Bridge11	-0.12
Top9	-0.54	Bridge13	0.24

Table S2

Table S2. The calculated adsorption energy of different sites for single Ca on B_5N_3

Site	E_{ads}(eV)	Site	E_{ads}(eV)
Hollow1	-0.39	Bridge1	-0.39
Hollow2	-0.39	Bridge2	-0.39
Hollow3	-0.39	Bridge3	0.30
Hollow4	-0.41	Bridge4	-0.39
Top1	-0.39	Bridge5	-0.39
Top2	-0.39	Bridge7	-0.39
Top3	0.30	Bridge8	-0.39
Top4	0.30	Bridge9	-0.39
Top5	-0.39	Bridge10	-0.39
Top8	-0.39	Bridge11	-0.39
Top9	-0.39	Bridge13	0.30

The Ca atoms on the Hollow 1 and Hollow 2 sites migrate to the Hollow 3 site after calculation. Therefore, the adsorption energies of H1 and H2 are equal to that of H3. Similarly, the adsorption energies of most top and bridge sites are also equal to the adsorption energies of H3 and H4 sites. And Ca atoms also migrate to the corresponding hollow site. The adsorption energies of T3, T4, B3 and B13 are positive, indicating that Ca atom cannot be adsorbed on these sites. Thus, all the calculations demonstrate that the potential sites of Ca system are H3 and H4 sites.

Table S3

Table S3. The calculated adsorption energy, charge transfer and distance between metal atom and B_5N_3

	E_{ads} (eV atom^{-1})	Q (|e|)	$d_{Metal-B5N3}$ (Å)
Ca	-0.41	1.24	2.05
Li	-0.54	0.78	1.55
Na	-0.22	0.64	2.14
K	-0.77	0.87	2.52

Table S4

Table S4. The calculated adsorption energy, charge transfer and distance between metal atoms and B_5N_3 for adsorption different Ca, Li, Na and K layers

Metal	Layer	Adsorption sites	Total numbers	E_{ads}(eV)	Q_{ave} (|e|)	Distance (Å)
Ca	One layer	H4	16	-0.45	0.77	2.04
		H3+H4	32	-0.01	0.47	2.08
	Two layers	H2+H3+H4	48	-0.07	0.29	2.11/5.28
		H1+H2+H3+H4	64	-0.24	0.22	2.12/5.68
Li	One layer	H3	16	-0.58	0.29	1.40
		H3+H4	32	-0.11	0.11	1.56
	Two layers	H2+H3+H4	48	0.13	\	1.48/2.06
Na	One layer	H3	16	-0.15	0.41	2.01
		H3+H4	32	-0.17	0.30	2.16
	Two layers	H2+H3+H4	48	-0.08	0.22	2.17/4.61
		H1+H2+H3+H4	64	-0.06	0.14	2.19/5.17
K	One layer	H3	16	-0.55	0.51	2.45
		H3+H4	32	0.21	\	2.59

[a] "/" means the bader charge are unavailable.

REFERENCES

1. B. Liang, N. Ma, Y. Wang, T. Wang and J. Fan, *Appl. Surf. Sci.*, 2022, **599**, 153927.