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

Supporting Information

Evolutionary structure predicted assisted design of anode materials for Ca-ion battery based on phosphorene

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1. Cartesian coordinates for the allotropes of phosphorene.

(A) α Pn

P	1.675407887	0.382691860	6.375204086
P	0.000000000	1.862238646	6.375204086
P	1.675407887	4.107169151	4.263043404
P	0.000000000	2.627622366	4.263043404

a=3.35 Å, b= 4.49 Å.

(B) β Pn

P 0.66481257 1.72061050 4.78454992

P -0.97963745 2.67011927 3.54986464

a=3.28897 Å, b= 3.28897 Å.

(C) γ Pn

P	0.00000000	0.08571784	10.35762000
P	0.00000000	2.42022295	10.35762000
P	1.63500000	2.84991784	11.84238000
P	1.63500000	5.18442295	11.84238000

a=3.27 Å, b= 5.528 Å.

(D) δ Pn

P	0.03061958	0.47983824	10.40284000
P	0.03061958	2.79288784	10.40284000
P	2.21229374	5.61129348	10.40284000
P	2.21229374	3.29823260	10.40284000
P	2.80061404	0.47983260	12.52716000
P	2.80061404	2.79289348	12.52716000

P	4.98228820	5.61128784	12.52716000
P	4.98228820	3.29823824	12.52716000

a=5.54 Å, b= 5.5368 Å.

(E) ζ Pn

P	0.58378578	3.69027624	6.74649000
P	2.30621422	3.69027624	8.25351000
P	5.19621422	5.63972376	6.74649000
P	3.47378578	5.63972376	8.25351000
P	5.19621422	2.52972376	8.25351000
P	3.47378578	2.52972376	6.74649000
P	0.58378578	0.58027624	8.25351000
P	2.30621422	0.58027624	6.74649000

a=5.78 Å, b= 6.22 Å.

2. Fully calcinated structures of alpha, gamma and delta phases of phosphorene.

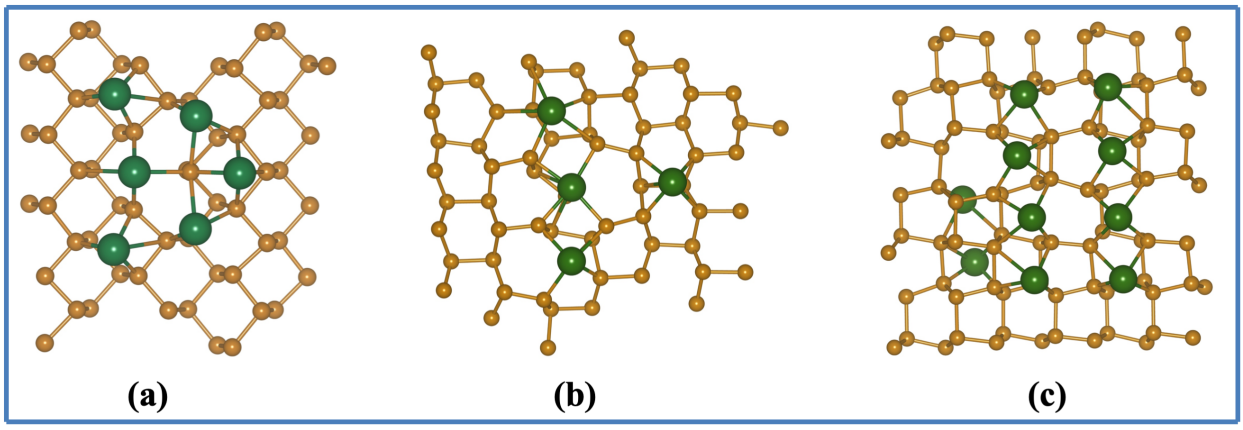

Figure S1: *Fully calcium intercalated (a) alpha ($Ca_{0.125}P$) (b)gamma ($Ca_{0.083}P$) and (c) delta-phases ($Ca_{0.139}P$) of phosphorene.*

3. Variation of binding energy with Ca content of δ-phase of phosphorene.

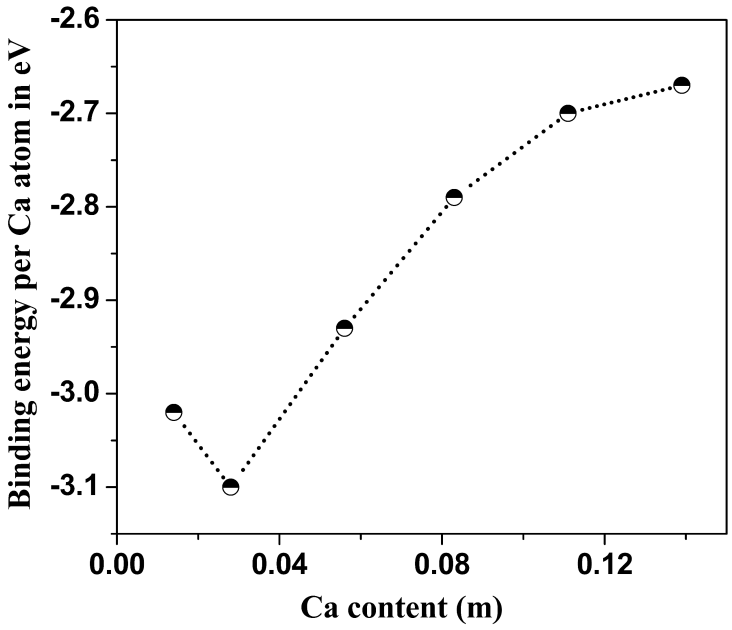

Figure S2: Variation of binding energy with Ca content of δ-phase of phosphorene.

4. Detailed minimum energy pathway for Ca diffusion along armchair and zigzag direction of α-allotrope.

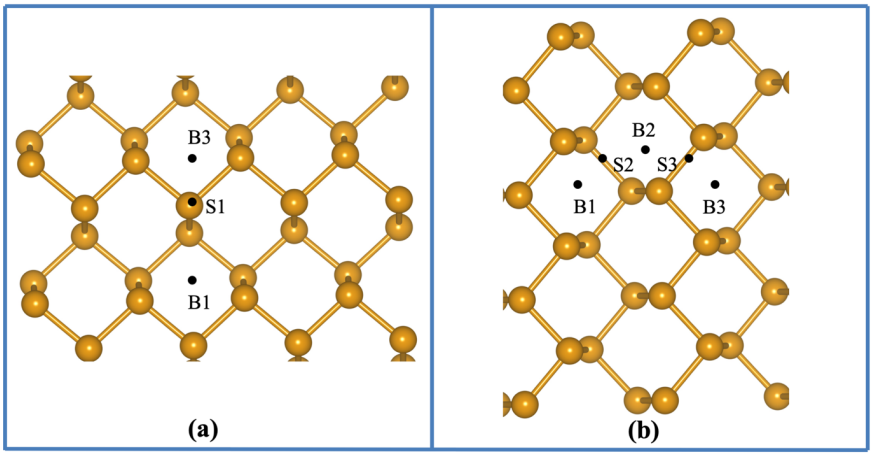

Figure S3: *Detailed minimum energy pathway for Ca diffusion along (a) armchair and (b) zigzag direction of α-allotrope.*

5. Detailed minimum energy pathway for Ca diffusion along zigzag direction of γ-phase.

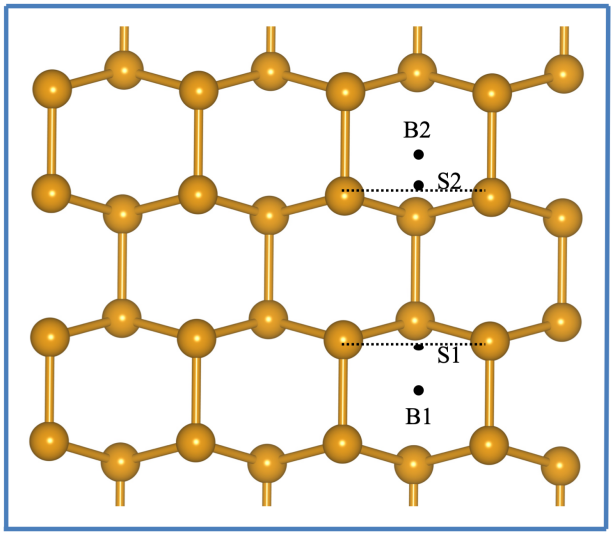

Figure S4: *Detailed minimum energy pathway for Ca diffusion along zigzag direction of γ-phase.*

6. Structures of saddle points during diffusion of Ca along zigzag direction of γ-allotrope.

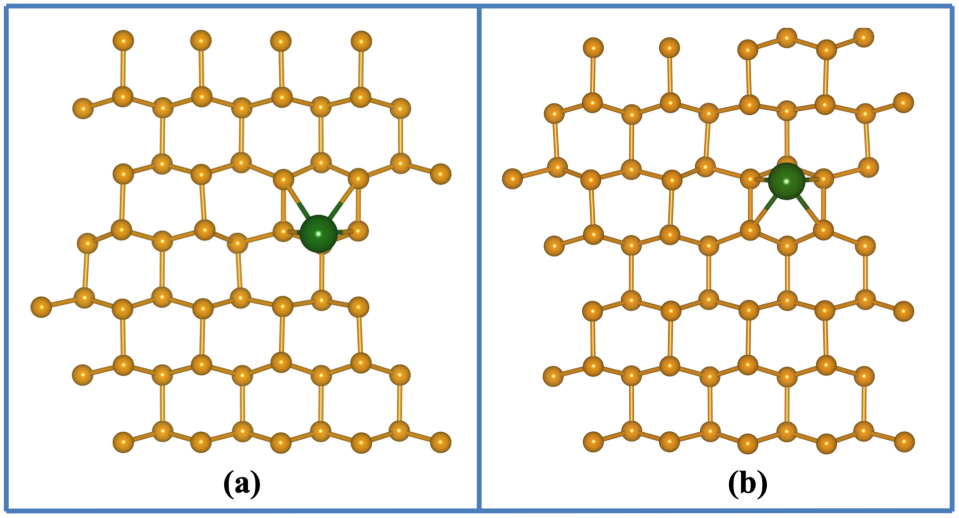

Figure S5: *Structures of saddle points during diffusion of Ca along zigzag direction of γ allotrope.*

7. Convergence test of k-point mesh for α-phase.

Table S1:

k-point grid	Binding energy of Ca (eV)
4 × 4 × 1	-2.47
5 × 5 × 1	-2.56
6 × 6 × 1	-2.57
7 × 7 × 1	-2.57

8. Cartesian co-ordinates for the structures generated using evolutionary structure prediction algorithm with lattice parameters and their corresponding energies calculated using plane wave methods (DFT-D2).

(A) Ca_3P_2

Ca	1.15787216	2.04312495	3.51284057
Ca	-1.21243905	3.37523322	5.92647873
Ca	3.52124304	0.69305972	1.10052338
P	3.45642802	0.65932947	5.13576165
P	-1.15249264	3.41000164	1.89283692

a=4.71587 Å, b= 4.67724 Å, c= 7.06422 Å; α= 90.01012°, β= 90.37836°, γ=119.66444°

(B) Ca_4P_4

Ca	3.53996500	1.24847404	1.42515848

Ca	1.75432561	2.88798059	6.27057140
Ca	-0.70083202	1.82703063	8.41881815
Ca	1.08728531	0.19583187	3.57674680
P	0.76903033	2.49117517	1.62606960
P	2.06712885	0.59418142	8.22343758
P	0.72005110	0.11943845	6.47468850
P	2.13234752	2.94530734	3.36984990

a=5.40778 Å, b= 4.34652 Å, c= 9.89737 Å; α= 88.64252°, β= 101.36213°, γ= 113.32098°

(C) Ca_4P_7

Ca	2.43790297	1.63109014	2.24649235
Ca	4.89066066	4.44336398	0.89155278
Ca	0.34790886	3.98183007	4.40389390
Ca	2.95420825	6.56919385	5.93952265
P	1.54885006	1.23747806	5.14160296
P	1.96770702	4.52512333	1.96137314
P	2.08493941	2.79519410	6.61037958
P	5.15645472	1.55999543	0.26268710
P	3.50280414	5.49559017	3.22926379
P	5.34513193	1.90943731	2.42031792
P	4.06142577	3.82922666	6.30830911

a=6.0205 Å, b= 5.858445 Å, c= 7.36062 Å; α= 79.61485°, β= 84.77111°, γ= 104.7499°

(D) Ca_4P_{12}

Ca	1.85884834	1.69035540	0.68039477
Ca	4.34027544	1.78972195	4.03322197
Ca	3.68179458	5.19632801	8.25901051
Ca	0.55540068	5.48701196	4.82032306
P	4.29303965	1.51282094	7.42753719
P	2.42073687	1.89949357	6.29955982
P	1.13844544	5.57178922	1.50840706
P	3.02821616	5.45302699	2.72776458
P	3.95486646	7.25046115	1.76534884
P	0.29556184	3.72378196	2.43016009
P	1.42706901	3.44108877	7.48613515
P	4.12683387	7.13289026	6.11379995
P	1.90642946	-0.23829308	6.76185625
P	5.20786590	3.26846986	6.48848787
P	3.92635182	3.69291687	1.66874164
P	0.31699858	7.35776711	2.54443631

a=5.7076 Å, b= 7.47315 Å, c= 8.89302 Å; α= 92.2923°, β= 92.92014°, γ= 89.69074°

9. Phonon spectrums of other two structures originated from evolutionary structure prediction algorithm.

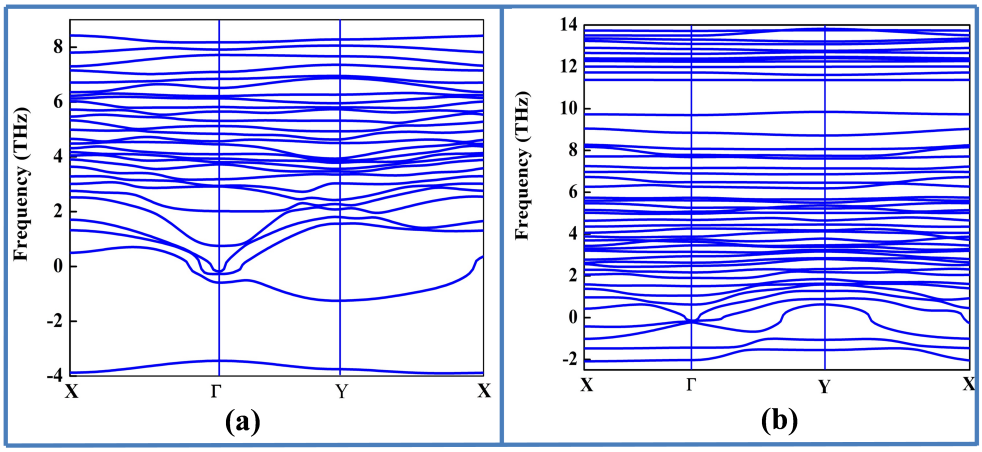

Figure S6: *Phonon dispersion curve of (a) Ca_4P_7 and (b) Ca_4P_{12} phases*

10. Convex curve taking possible phases of all the 2319 structures.

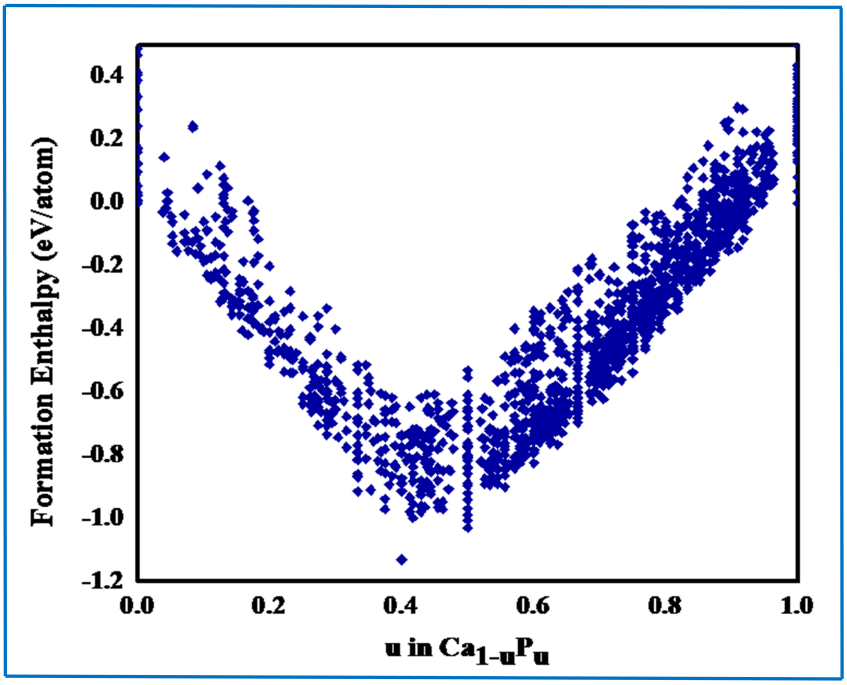

Figure S7: *Convex curve taking all possible 2319 structures.*

11. RMSD plots for Ca_3P_2 and Ca_4P_4

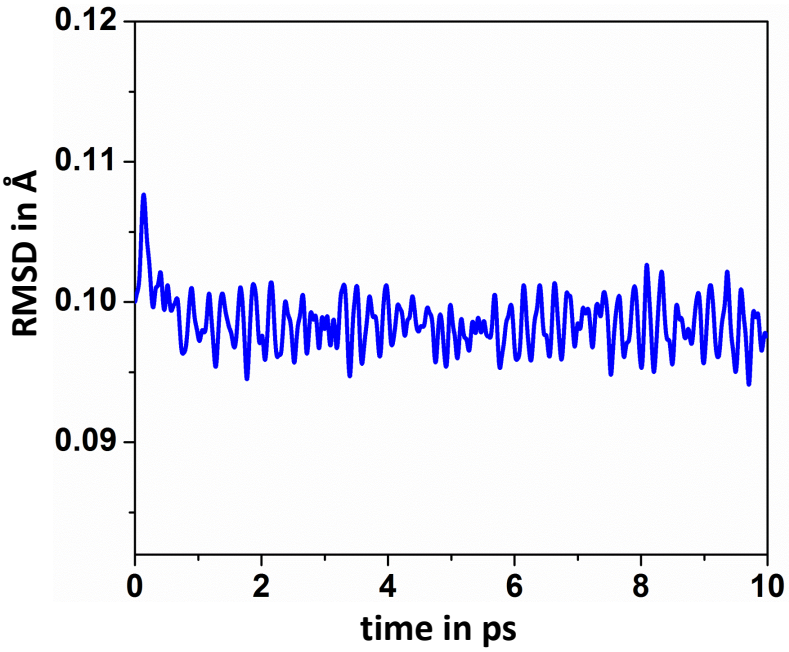

Figure S8: Plot of RMSD with time for Ca_3P_2 at 300 K.

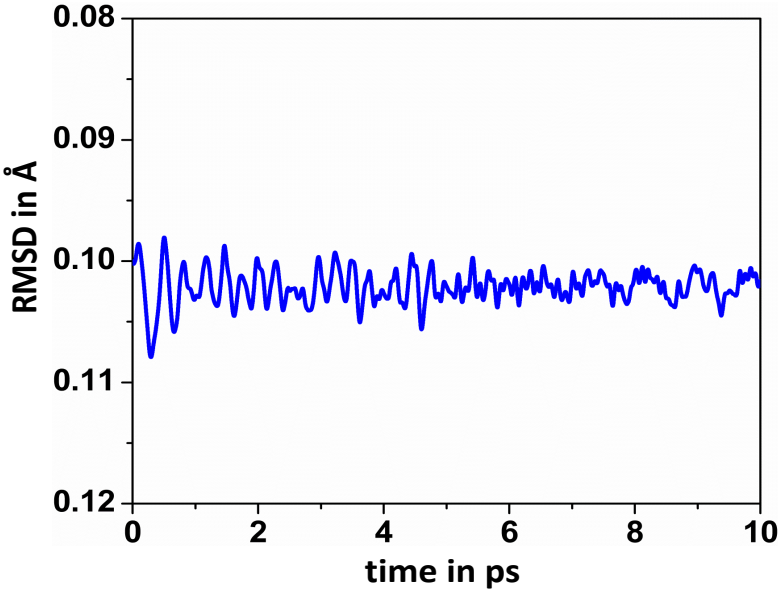

Figure S9: RMSD plot for Ca_4P_4 at 300 K.