Supporting Information

A novel 2D VC_4 as a promising Na-host material for Na-ion batteries: computational insights

Javed Rehman[3#], Jiayu Gao[1#], Tong Yu[2*], Adel El-marghany[4], Guochun Yang[1*]

1. State Key Laboratory of Metastable Materials Science & Technology and Key Laboratory for Microstructural Material Physics of Hebei Province, School of Science, Yanshan University, Qinhuangdao 066004, China
2. Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Sciences, Shenyang 110016, China
3. State Key Laboratory of Metastable Materials Science and Technology, and School of Materials Science and Engineering, Yanshan University, Qinhuangdao 066004, China
4. Department of Chemistry, College of Science, King Saud University, P.O. Box 2455, Riyadh 11451, Saudi Arabia

Correspondence should be addressed to:

* tyu@imr.ac.cn (T. Yu) and yanggc468@nenu.edu.cn (G. Yang)

[#]Javed Rehman and Jiayu Gao contributed equally to this work.

Computational Details

The particle swarm optimization (PSO) method within the evolutionary algorithm as implemented in the Crystal structure Analysis by Particle Swarm Optimization (CALYPSO) code[1] was employed to find the lowest energy structures of VC_4 monolayers. Unit cells containing 1, 2, and 4 formula units (f.u.) were considered. In the first step, random structures with certain symmetries are built, in which atomic coordinates are generated by the crystallographic symmetry operations. Local optimizations using the VASP code were done with the conjugate gradients method and stopped when Gibbs free energy changes became smaller than 1×10^{-5} eV per cell. After processing the first-generation structures, 60% of them with lower Gibbs free energies are selected to construct the next generation structures by PSO. 40% of the structures in the new generation are randomly generated. A structure fingerprinting technique of bond characterization matrix is applied to the generated structures, so that identical structures are strictly forbidden. These procedures significantly enhance the diversity of the structures, which is crucial for structural global search efficiency. In most cases, structural searching simulations for each calculation were stopped after generating 1000 ~ 1200 structures (e.g., about 20 ~ 30 generations).

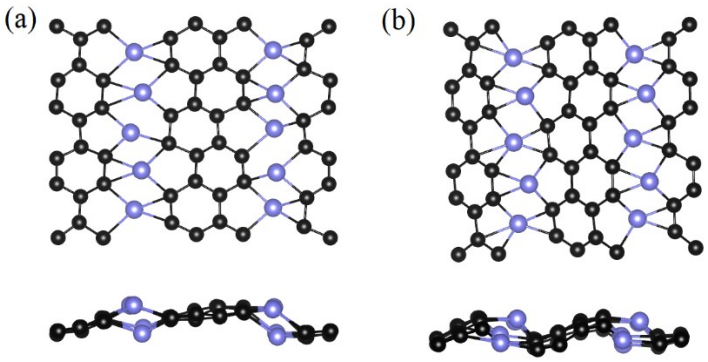

Fig. S1 Structures of VC_4 after 10 ps steps of AIMD at (a) 500 K and (b) 1000 K.

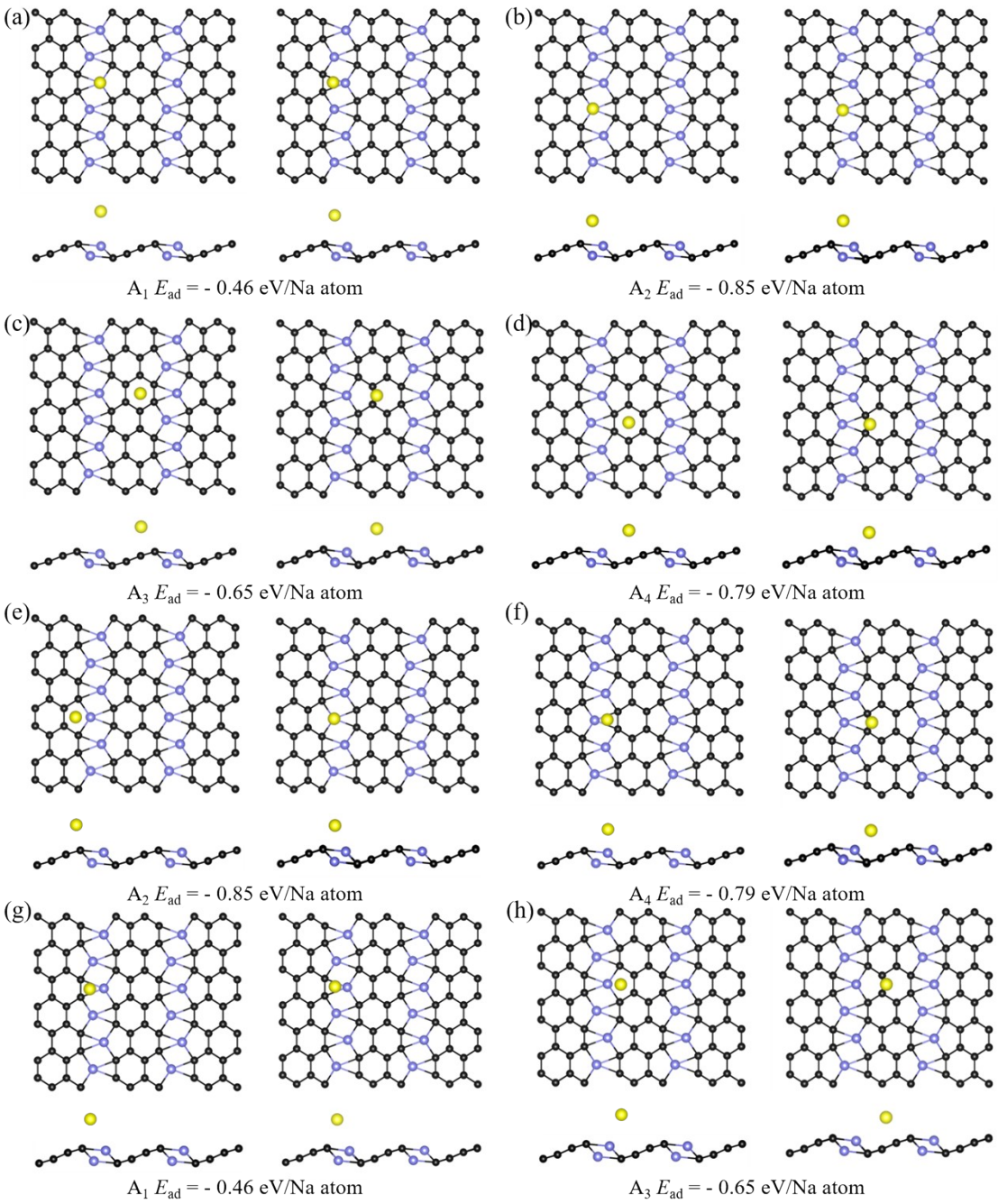

Fig. S2 Adsorption of Na on monolayer VC_4 at (a) A_1-site, (b) A_2-site, (c) A_3-site, (d) A_4-site, (e) A_2-site, (f) A_4-site, (g) A_1-site, and (h) A_3-site.

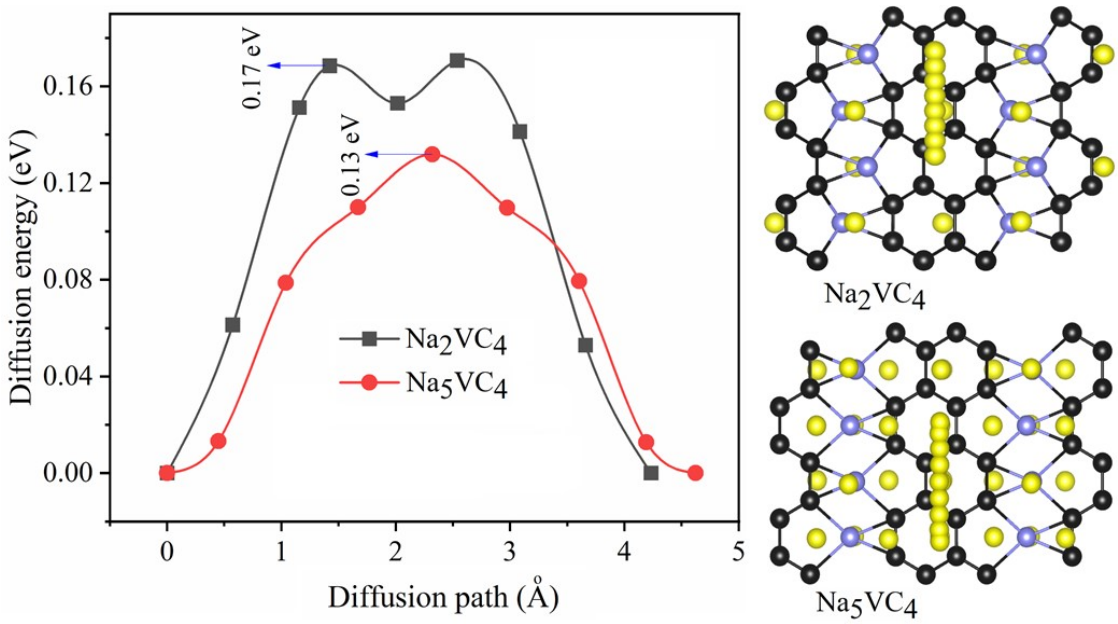

Fig. S3 Diffusion energy barrier and their corresponding path of Na_xVC_4 at $x = 2$ and 5.

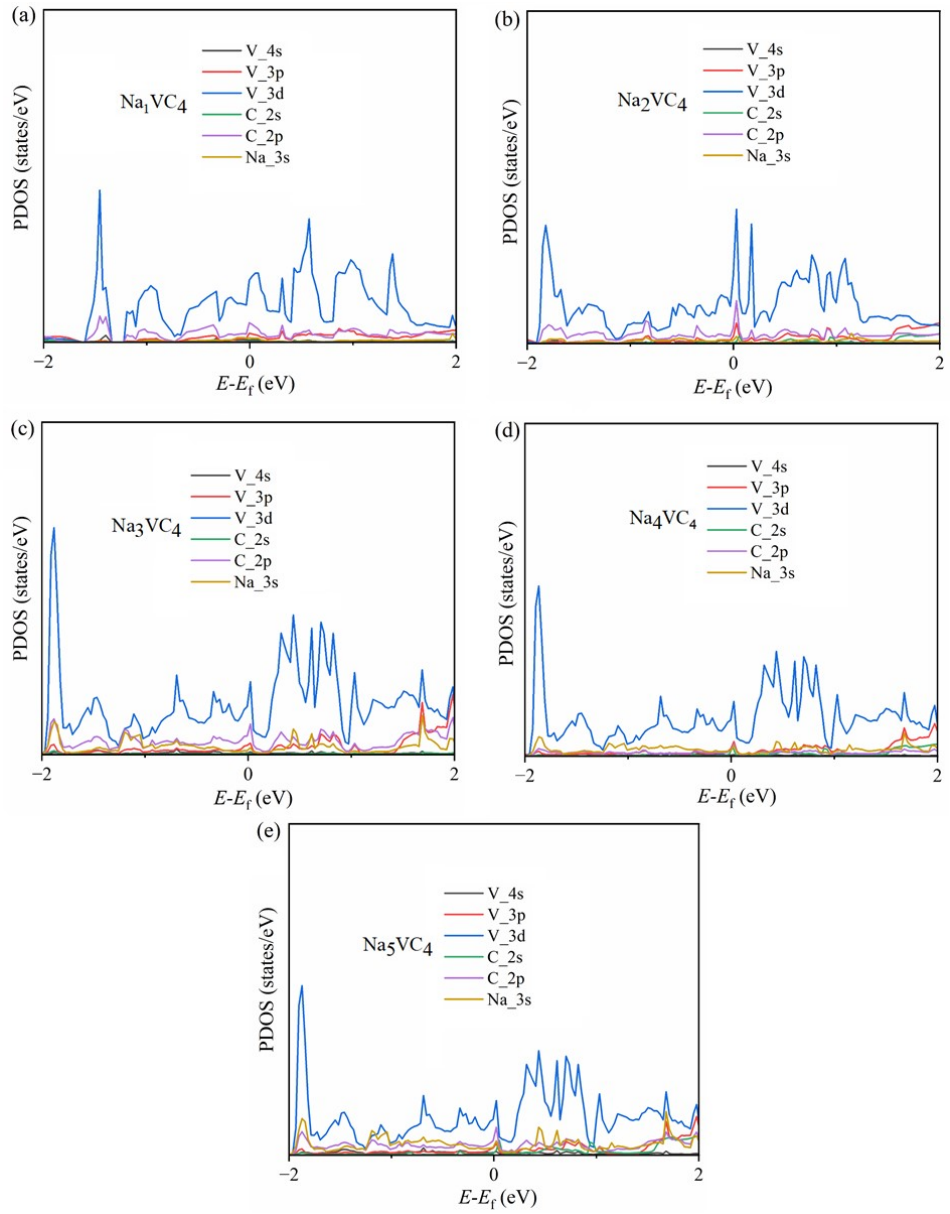

Fig. S4 Partial density of states of (a) Na_1VC_4, (b) Na_2VC_4, (c) Na_3VC_4, (d) Na_4VC_4, and (e) Na_5VC_4.

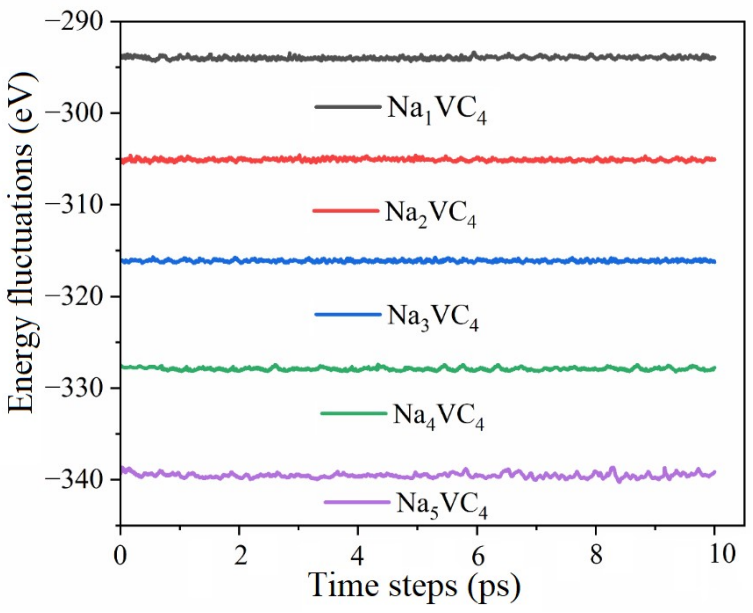

Fig. S5 Energy fluctuations versus time steps of Na_xVC_4 (x = 1, 2, 3, 4, and 5) at 300 K after 10 ps.

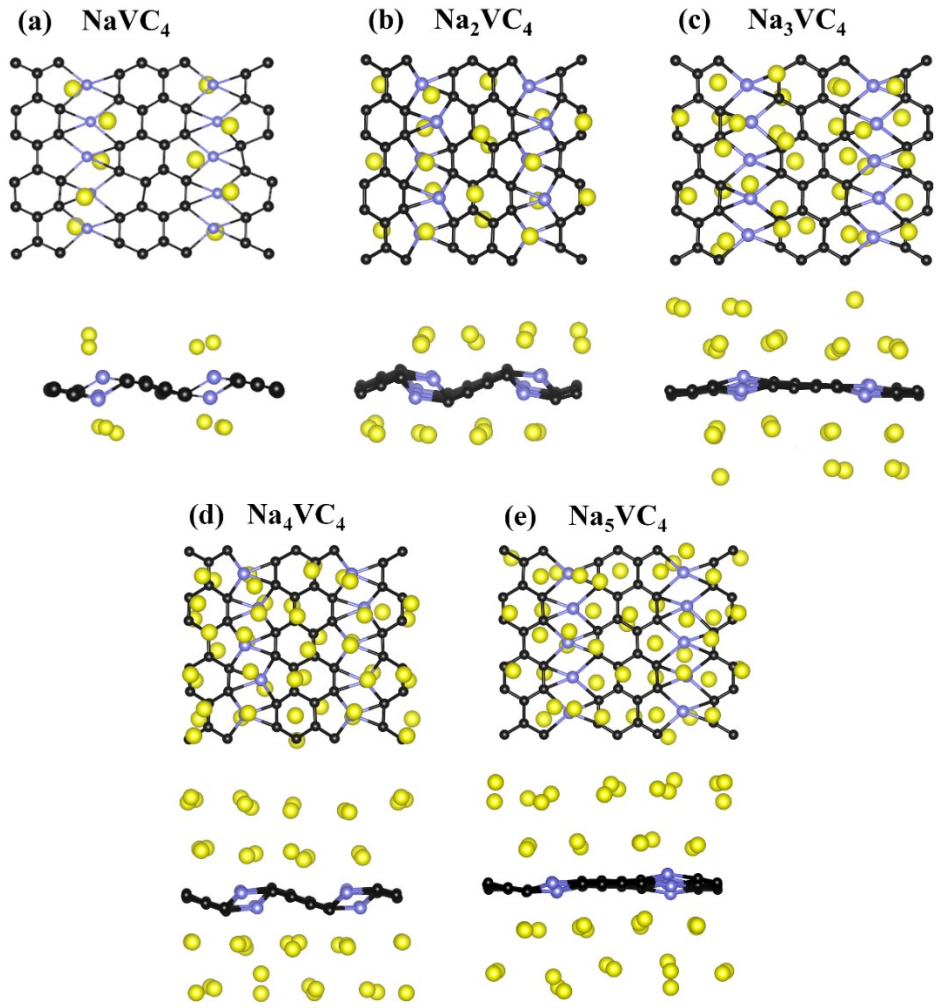

Fig. S6 Structural snapshots of Na_xVC_4 (x = 1, 2, 3, 4, and 5) at 300 K after 10 ps.

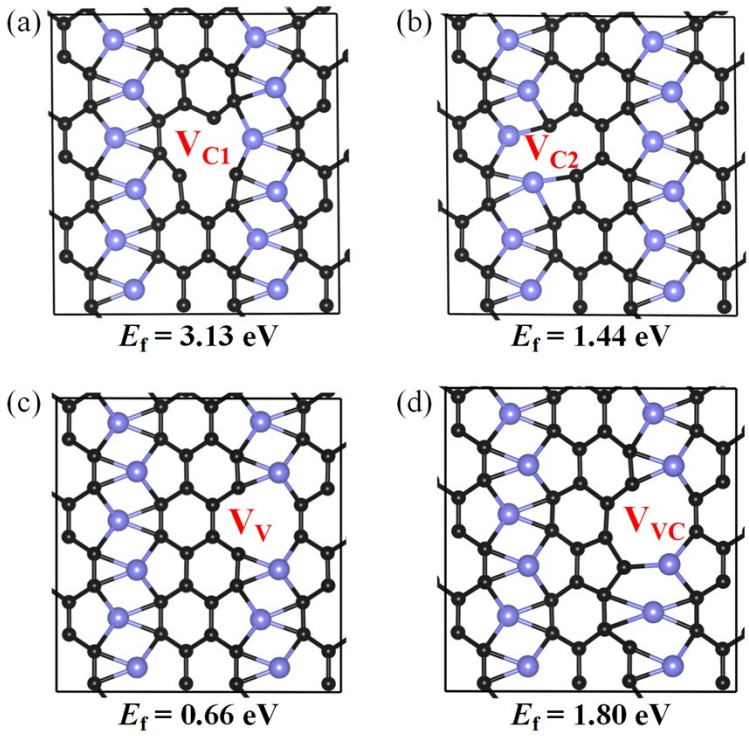

Fig. S7 Optimized geometry of various defects in VC_4 monolayer. (a) V_{C1}, (b) V_{C2}, (C) V_V, (d) V_{VC} vacancy.

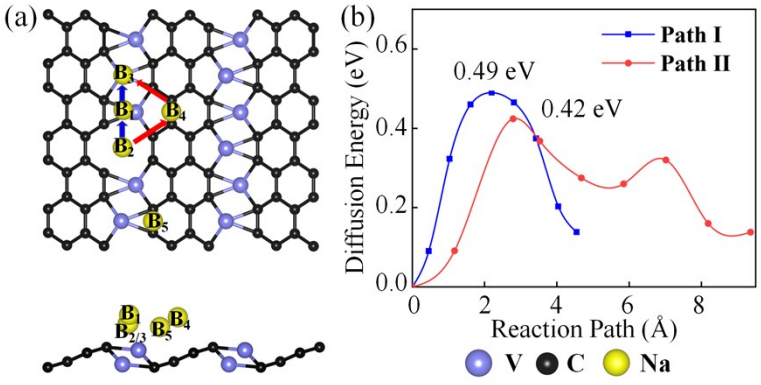

Fig. S8 (a) The inequivalent adsorption sites of 2D VC_4 with Vv vacancy, named as B_1, B_2, B_3, B_4, and B_5. The side view of B_2 and B_3 are denoted as $B_{2/3}$ due to their close positions in the z direction. The considered migration paths of Na diffusion on the 2D VC_4 with Vv vacancy. (b) The corresponding diffusion energy barrier profiles of path I and path II.

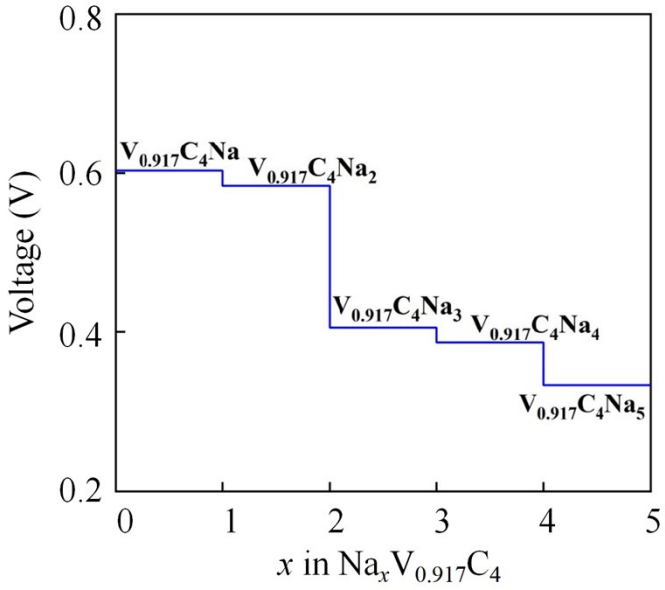

Fig. S9 Average voltages of different Na concentrations in $Na_xV_{0.917}C_4$ (x = 1-5).

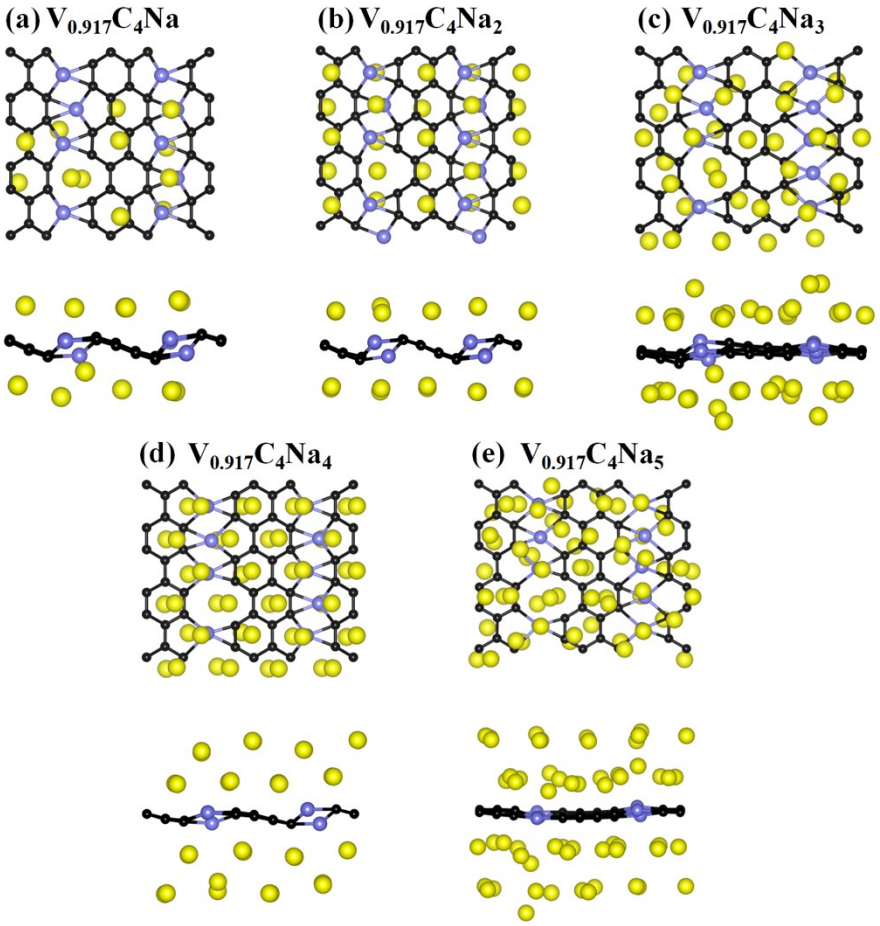

Fig. S10 Optimized structures of $Na_xV_{0.917}C_4$ (x = 1-5).

Table S1 Comparative study of the calculated voltage, energy barrier, and Na storage capacity of VC_4 monolayer with previously reported 2D materials.

Material	Voltage (V)	Diffusion barrier (eV)	Capacity (mAh g^{-1})	Ref.
Li-CuC_6	0.34	0.41	1188	[2]
Li-Mo_2C	0.14	0.13	526	[3]
Li-VC_2	0.40	0.09	1430	[4]
K-SnC	0.41	0.17	410	[5]
K-PC_6	0.64	0.29	780	[6]
Na-CP_3	0.53	0.35	2298	[7]
Na-ZrC_2	0.25	0.02	932	[8]
Na-TiC_3	0.18	0.20	1278	[9]
Li-NiC_3	0.17	0.50	1698	[10]
Na-V_2C	0.49	0.14	300	[11]
Na-Twin-Graphene	1.09	0.198	496	[12]
Na_xVC_4	0.51	0.32	1353	This work

Table S2 Adsorption energies of Na at different sites on $V_{0.917}C_4$ monolayer.

Site	Adsorption energies (eV/Na atom)
B_1-site	- 0.73
B_2-site	- 0.82
B_3-site	- 0.65
B_4-site	- 0.48
B_5-site	- 0.61

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