Supporting Information for

# Nitrogen Coordination-Regulated Electronic Structure of V-Based Single-Atom M-N-C for Efficient Sodium Storage

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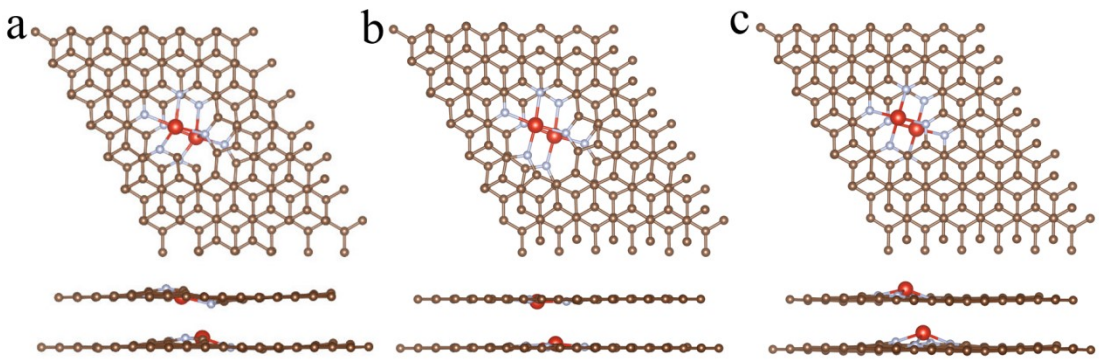


Figure S1. Optimized structures for the three selected V-$N_4$-G bilayer configurations. (a) V-$N_{1pyr}$-$N_{3pyd}$-G bilayer, (b) V-$N_{2pyr}$-$N_{2pyd}$-G bilayer in horizontal, and (c) V-$N_{4pyd}$-G bilayer.

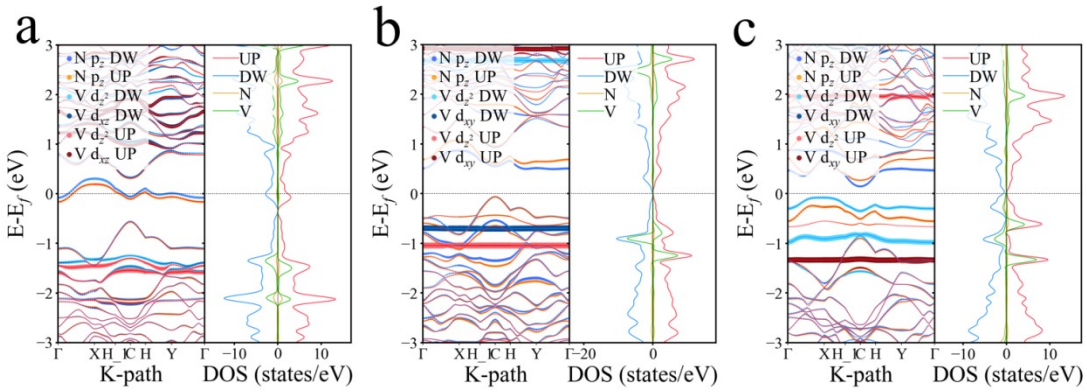


Figure S2. Spin-polarized electronic band structure and density of states (DOS) for the configurations: (a) V-$N_{1pyr}$-$N_{3pyd}$-G, (b) V-$N_{2pyr}$-$N_{2pyd}$-G(H), and (c) V-$N_{4pyd}$-G calculated in vacuum. The left panels show band structures with the Fermi level set at 0 eV. The right panels display the corresponding total and projected density of states (PDOS). Red lines represent up-spin (UP) states and blue lines represent down-spin (DW) states. Contributions from the V atom's $d_{xz}$, $d_{xy}$ and $d_z^2$ orbital and N atom's $p_z$ orbital are highlighted by colored symbols.

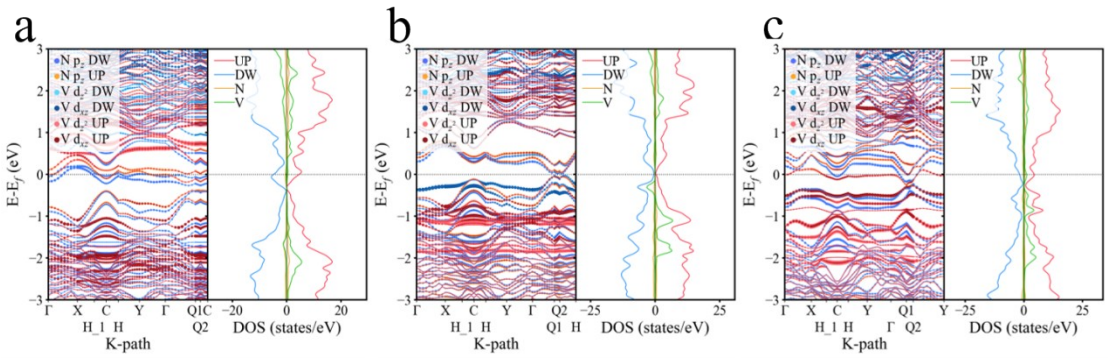


Figure S3. Spin-polarized electronic band structure and density of states (DOS) for the configurations: (a) V-$N_{1pyr}$-$N_{3pyd}$-G bilayer, (b) V-$N_{2pyr}$-$N_{2pyd}$-G(H) bilayer, and (c) V-$N_{4pyd}$-G bilayer calculated in vacuum. The left panels show band structures with the Fermi level set at 0 eV. The right panels display the corresponding total and projected density of states (PDOS). Red lines represent up-spin (UP) states and blue lines represent down-spin (DW) states. Contributions from the V atom's $d_{xz}$, $d_{xy}$ and $d_z^2$ orbital and N atom's $p_z$ orbital are highlighted by colored symbols.

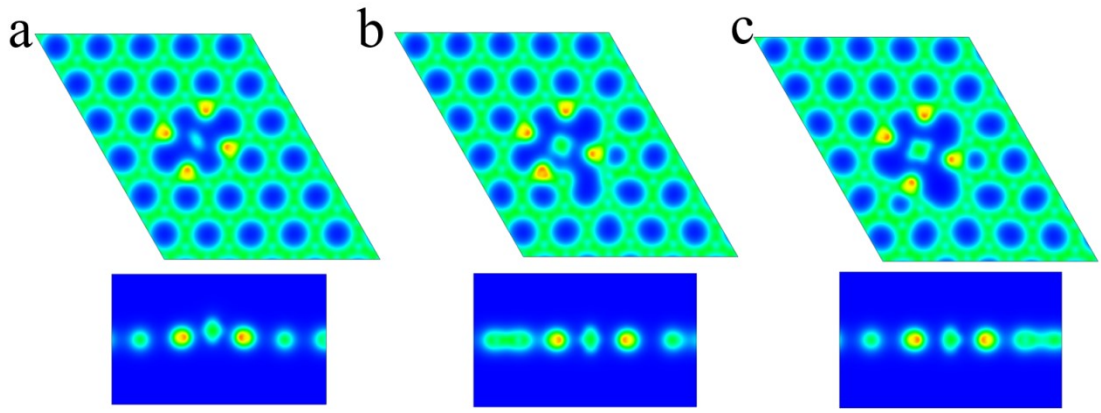


Figure S4. The electron density distributions for (a) V-$N_{4pyd}$-G, (b) V-$N_{1pyr}$-$N_{3pyd}$-G, and (c) V-$N_{2pyr}$-$N_{2pyd}$-G(H) configurations calculated in vacuum. The top row displays the top-view electron density maps across the graphene plane, while the bottom row shows the side-view perspective cross-sections through the central vanadium atom and two nitrogen atoms.

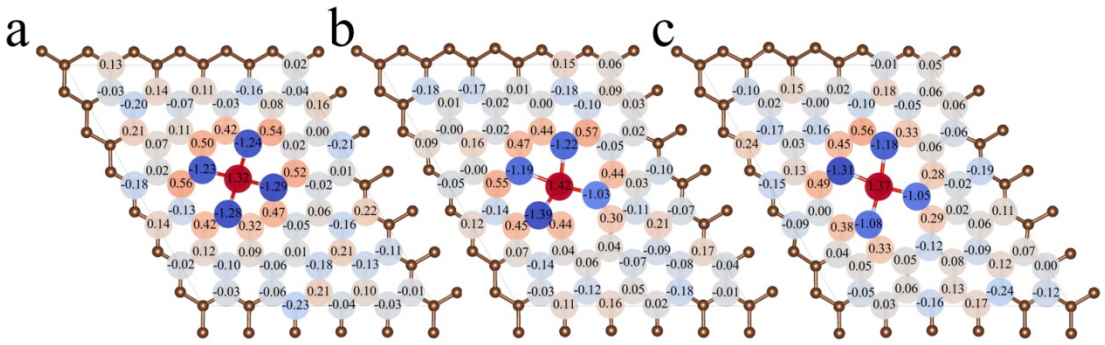


Figure S5. Bader charge analysis showing the charge distribution in (a) V-$N_{4pyd}$-G, (b) V-$N_{1pyr}$-$N_{3pyd}$-G, and (c) V-$N_{2pyr}$-$N_{2pyd}$-G(H) configurations calculated in vacuum. The numbers indicate the charge transfer values (in e), with positive values (orange/red) representing electron loss and negative values (blue) representing electron gain.

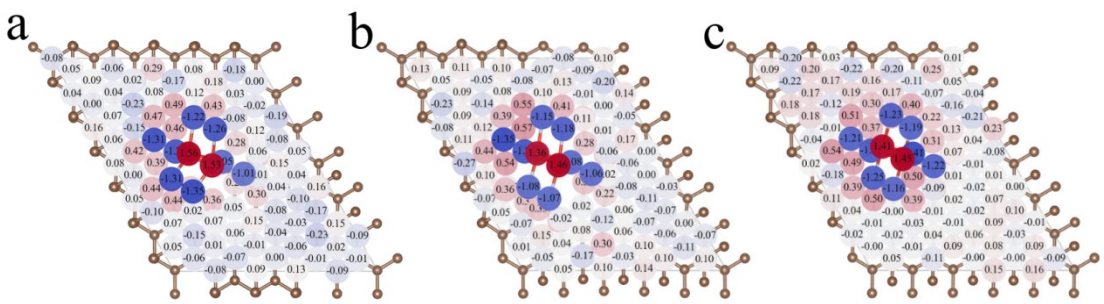


Figure S6. Bader charge analysis showing the charge distribution in (a) V-$N_{1pyr}$-$N_{3pyd}$-G bilayer, (b) V-$N_{2pyr}$-$N_{2pyd}$-G(H) bilayer and (c) V-$N_{4pyd}$-G bilayer configurations with the implicit solvation model. The numbers indicate the charge transfer values (in e), with positive values (red) representing electron loss and negative values (blue) representing electron gain.

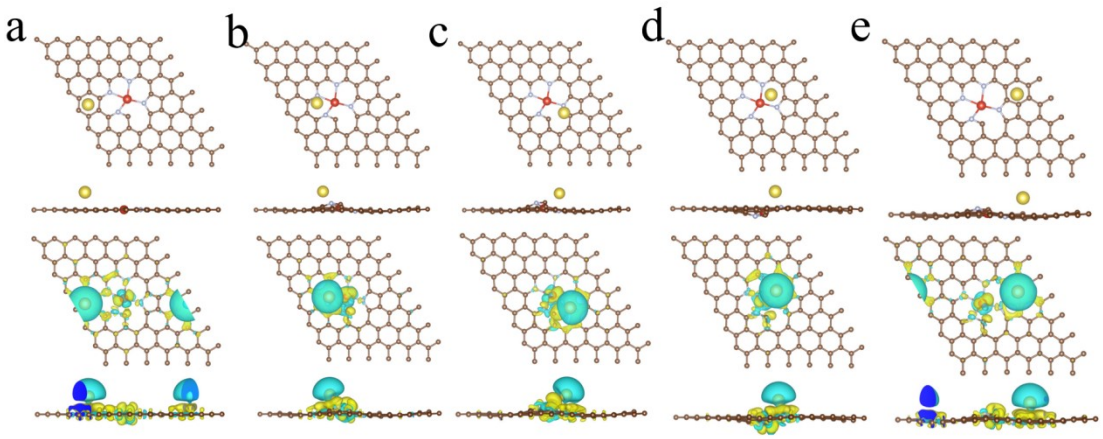


Figure S7. (a-e) Five sodium adsorption sites on V-$N_{1pyr}$-$N_{3pyd}$-G calculated in vacuum. Top and side views are shown for each structure. Brown, white, red, light red, pink and yellow spheres represent carbon, nitrogen, vanadium, oxygen, hydrogen and sodium atoms, respectively. Charge density difference plots, cyan regions represent electron depletion, while yellow regions represent electron accumulation. Isosurface value is set at 0.001 e/Å$^3$.

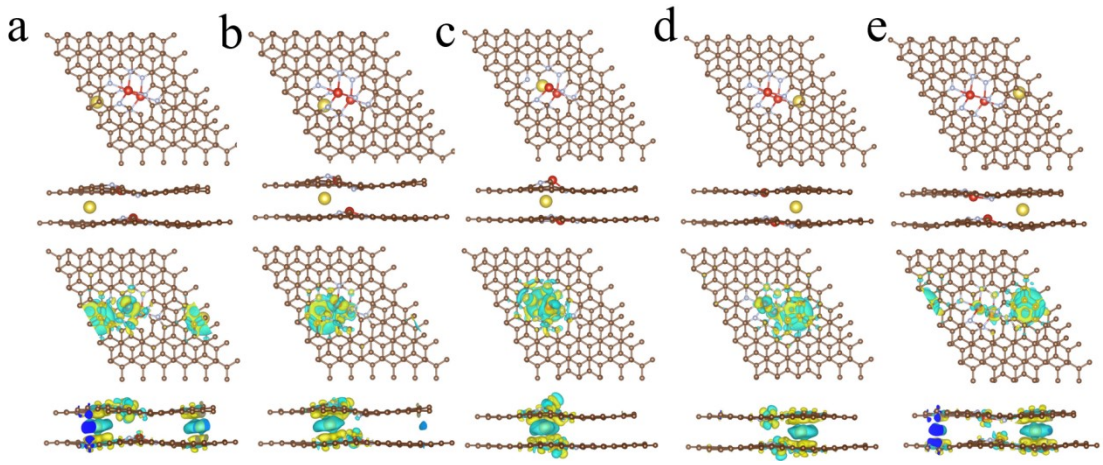


Figure S8. (a-e) Five sodium adsorption sites on V-$N_{1pyr}$-$N_{3pyd}$-G bilayer calculated in vacuum. Top and side views are shown for each structure. Brown, white, red, light red, pink and yellow spheres represent carbon, nitrogen, vanadium, oxygen, hydrogen and sodium atoms, respectively. Charge density difference plots, cyan regions represent electron depletion, while yellow regions represent electron accumulation. Isosurface value is set at 0.001 e/Å$^3$.

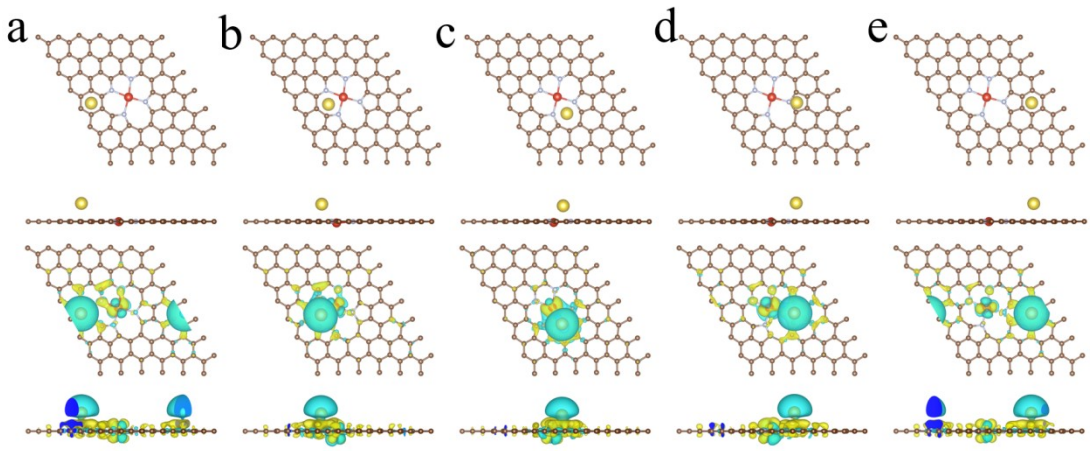


Figure S9. (a-e) Five sodium adsorption sites on V-$N_{2pyr}$-$N_{2pyd}$-G(H) calculated in vacuum. Top and side views are shown for each structure. Brown, white, red, light red, pink and yellow spheres represent carbon, nitrogen, vanadium, oxygen, hydrogen and sodium atoms, respectively. Charge density difference plots, cyan regions represent electron depletion, while yellow regions represent electron accumulation. Isosurface value is set at 0.001 e/Å$^3$.

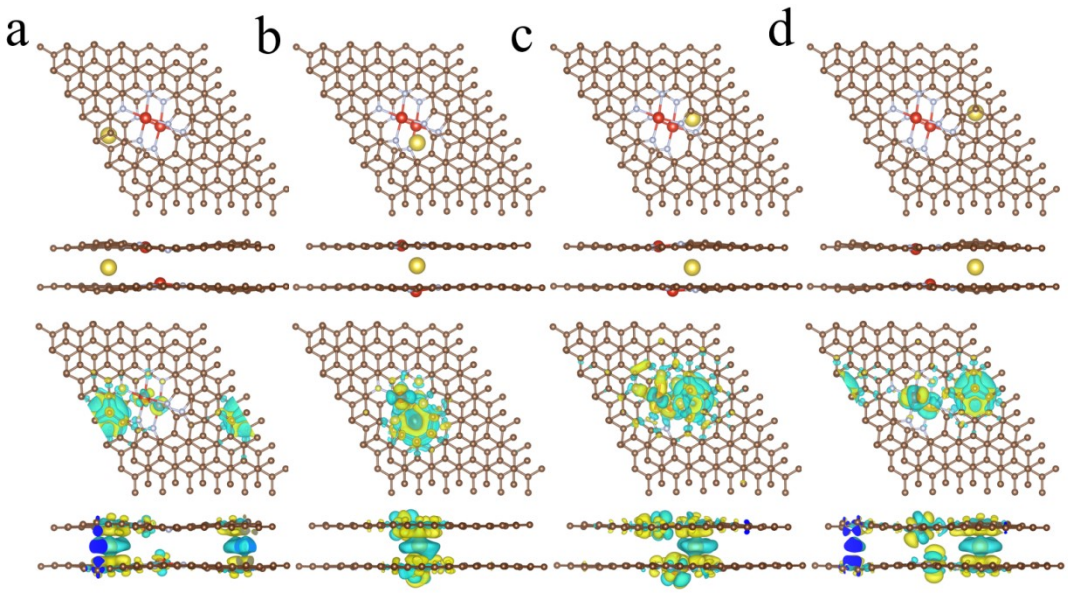


Figure S10. (a-d) Four sodium adsorption sites on V-$N_{2pyr}$-$N_{2pyd}$-G(H) bilayer calculated in vacuum. Top and side views are shown for each structure. Brown, white, red, light red, pink and yellow spheres represent carbon, nitrogen, vanadium, oxygen, hydrogen and sodium atoms, respectively. Charge density difference plots, cyan regions represent electron depletion, while yellow regions represent electron accumulation. Isosurface value is set at 0.001 e/Å$^3$.

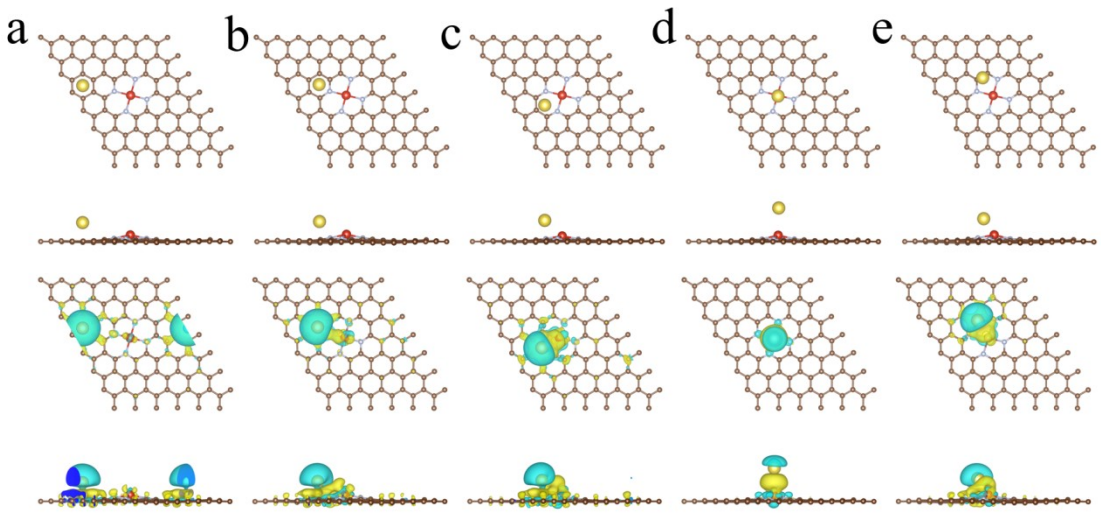


Figure S11. (a-e) Five sodium adsorption sites on V-$N_{4pyd}$-G calculated in vacuum. Top and side views are shown for each structure. Brown, white, red, light red, pink and yellow spheres represent carbon, nitrogen, vanadium, oxygen, hydrogen and sodium atoms, respectively. Charge density difference plots, cyan regions represent electron depletion, while yellow regions represent electron accumulation. Isosurface value is set at 0.001 e/Å$^3$.

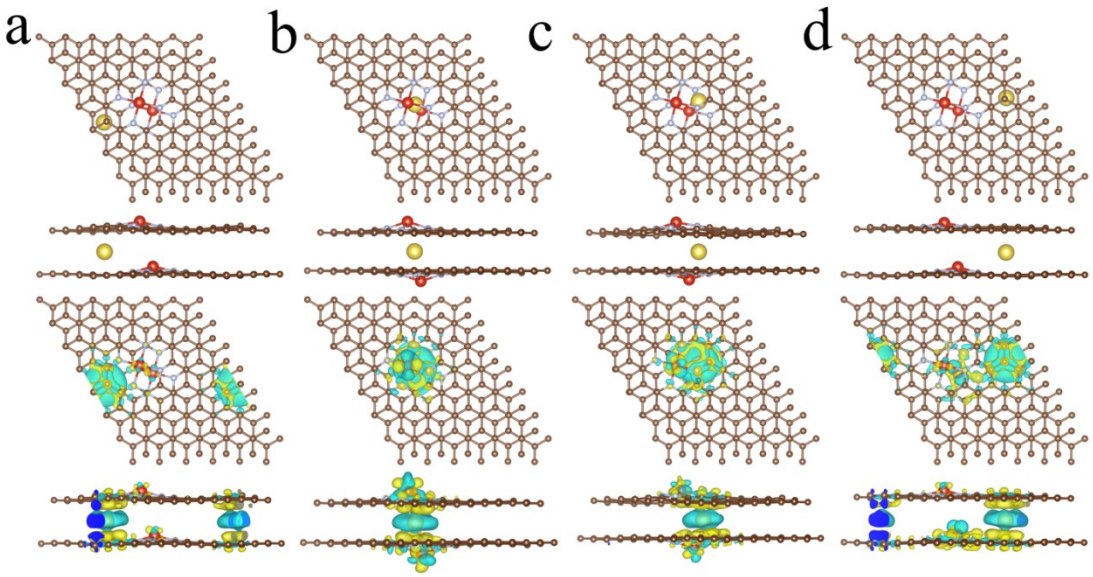


Figure S12. (a-d) Four sodium adsorption sites on V-$N_{4pyd}$-G bilayer calculated in vacuum. Top and side views are shown for each structure. Brown, white, red, light red, pink and yellow spheres represent carbon, nitrogen, vanadium, oxygen, hydrogen and sodium atoms, respectively. Charge density difference plots, cyan regions represent electron depletion, while yellow regions represent electron accumulation. Isosurface value is set at 0.001 e/Å$^3$.

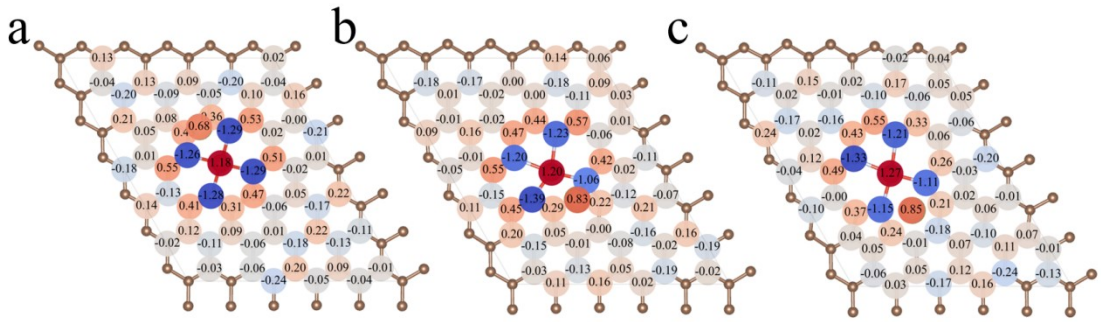


Figure S13. Bader charge analysis after sodium adsorption in (a) V-$N_{4pyd}$-G, (b) V-$N_{1pyr}$-$N_{3pyd}$-G, and (c) V-$N_{2pyr}$-$N_{2pyd}$-G(H) configurations calculated in vacuum. The numbers indicate the charge transfer values (in e), with positive values (orange/red) representing electron loss and negative values (blue) representing electron gain.

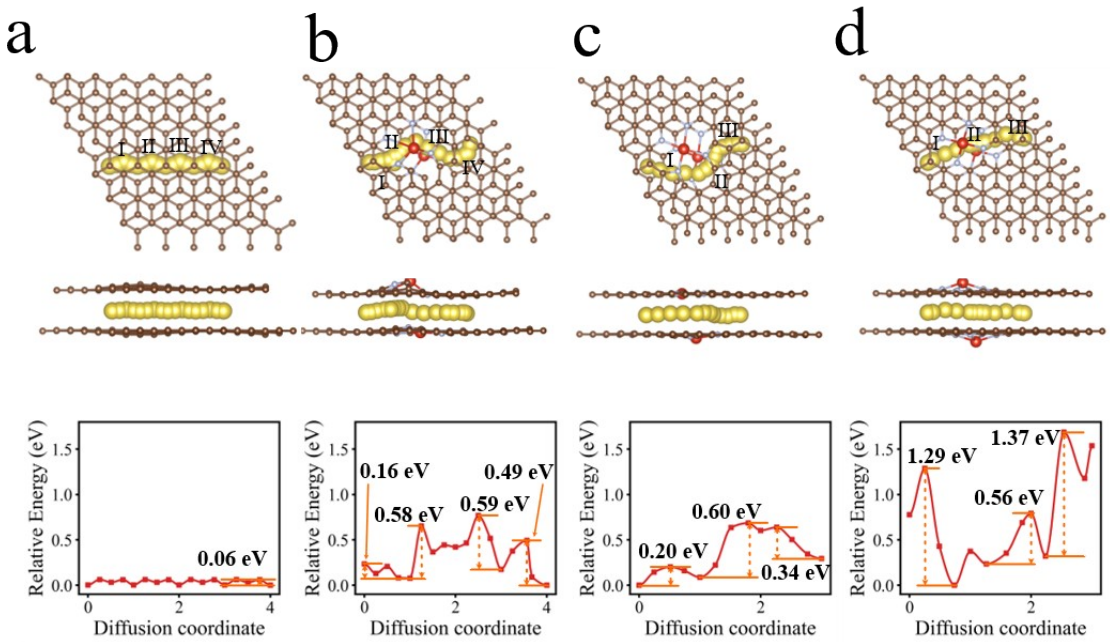


Figure S14. Energy diffusion barriers for sodium diffusion across duble layer (a) graphene (b) V-$N_{1pyr}$-$N_{3pyd}$-G (c) V-$N_{2pyr}$-$N_{2pyd}$-G(H) (d) V-$N_{4pyd}$-G configurations. The x-axis represents the reaction coordinate along the diffusion pathway, and the y-axis shows the relative energy in eV. Images on the left show the sodium diffusion pathways (yellow spheres) with labeled paths (I, II, III, IV), while right panels present the corresponding energy profiles along the diffusion coordinates.

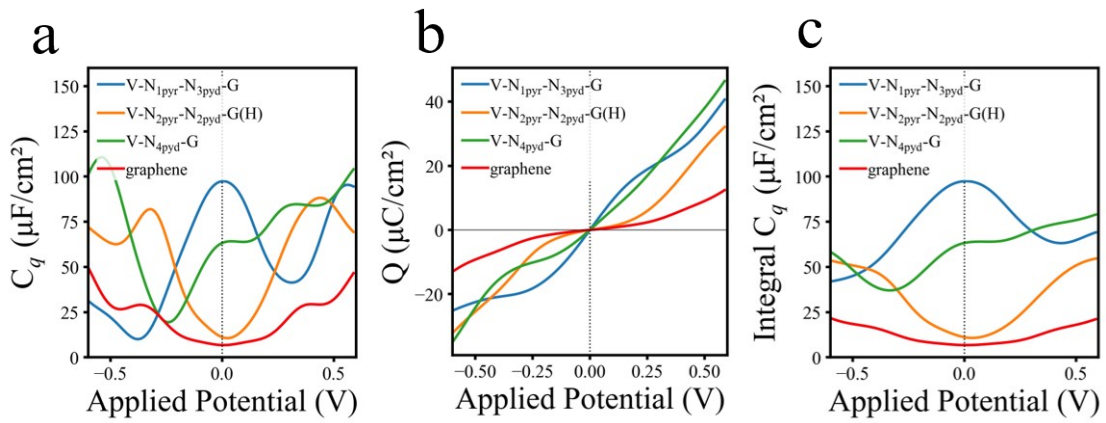


Figure S15. Quantum capacitance characteristics of V-$N_{4pyd}$-G bilayer (green), V-$N_{1pyr}$-$N_{3pyd}$-G bilayer (blue), V-$N_{2pyr}$-$N_{2pyd}$-G(H) bilayer (orange), and graphene bilayer (red) materials: (a) Differential quantum capacitance, (b) Surface charge (Q), and (c) Integral quantum capacitance as functions of applied potential.

Table S1. The formation energies calculated with and without implicit solvation for the three selected configurations.

| Materials | $E_f$ with solvation (eV) | $E_f$ without solvation (eV) |
|---|---|---|
| V-$N_{4pyd}$-G | −2.35 | −3.43 |
| V-$N_{1pyr}$-$N_{3pyd}$-G | −0.03 | −0.15 |
| V-$N_{2pyr}$-$N_{2pyd}$-G(H) | −0.13 | −1.19 |

Table S2. The formation energies with and without implicit solvation for the three selected V-N4-G bilayer configurations.

| Materials | $E_f$ with solvation (eV) | $E_f$ without solvation (eV) |
|---|---|---|
| V-$N_{4pyd}$-G bilayer | −9.19 | −9.02 |
| V-$N_{1pyr}$-$N_{3pyd}$-G bilayer | −2.21 | −1.96 |
| V-$N_{2pyr}$-$N_{2pyd}$-G(H) bilayer | −4.01 | −3.86 |

Table S3. Magnetic moments ($\mu_B$) on the vanadium atom in single-layer V-$N_4$-G configurations before and after Na adsorption.

| Materials | Magnetic moment before Na ($\mu_B$) | Magnetic moment after Na ($\mu_B$) | Change ($\Delta\mu$) |
|---|---|---|---|
| V-$N_{4pyd}$-G | 0.818 | 2.806 | 1.988 |
| V-$N_{1pyr}$-$N_{3pyd}$-G | 0.025 | 2.682 | 2.657 |
| V-$N_{2pyr}$-$N_{2pyd}$-G(H) | 0.876 | 2.510 | 1.634 |