Electronic Supplementary Material (ESI) for Nanoscale.

Lithium Intercalation in Two-Dimensional Penta-NiN_2: Insights from NiN_2/NiN_2 Homostructure and G/NiN_2 Heterostructure †

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1. Structural Properties and Electronic Band Structure of NiN_2

Nickel diazenide (NiN_2) is a pentagonal two-dimensional (2D) hybrid layer of nickel (Ni) and nitrogen (N) atoms in a crystalline lattice consisting of Ni_2N_3 5-membered rings arranged side by side (Figure S1) [1]. In NiN_2, the properties and characteristics of the material are dominantly affected by the nitrogen bonds. As depicted in Figure S1, the trigonal planar arrangement of the nitrogen atoms results in their sp^2 hybridized

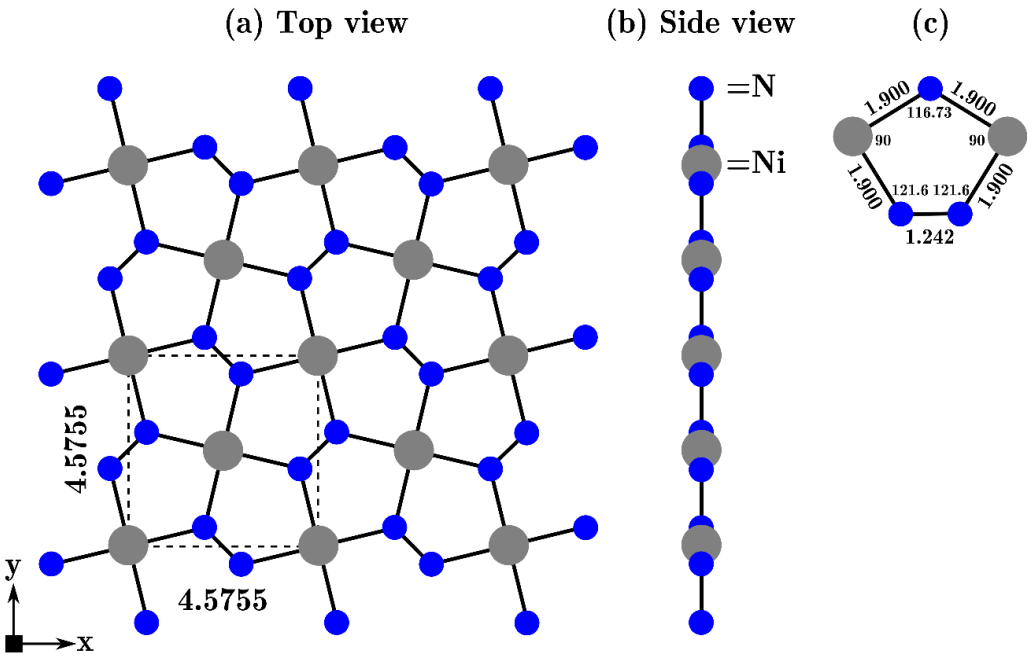

Figure S1. Crystal structure of NiN_2 from (a) top and (b) side views. (c) Geometry configuration of a single Ni_2N_3 pentagon. Gray and blue spheres represent Ni (= nickel) and N (= nitrogen) atoms, respectively. Numbers show interatomic distances (in Å) and bond angles (in degrees).

orbitals and double covalent bonds between the nitrogen atoms (N=N). This yields good mechanical strength for NiN_2, approximately one-third to half that of graphene [2]. Furthermore, the nitrogen-rich nature of NiN_2 offers plenty of electrochemically active sites that can participate in electron transfer processes. An important characteristic of NiN_2 is its transition from a metallic behavior in bulk form to a direct-band-gap semiconductor in its single-layer form. From Figure S2a, in bulk NiN_2, the occupied electronic band near the Fermi energy is mainly formed by *d* orbitals of Ni atoms overlapping with *p* orbitals of N atoms. However, once the layers are reduced to a single layer, a direct energy gap of ~1 eV is observed (Figure S2b).

2. Electronic Band Structure of NiN_2/NiN_2 and Average Displacement Analysis (ADA) under Different Lithium Intercalation Concentrations

Figure 3Sa-c illustrates the electronic band structure of a bilayer NiN_2, with lithium atoms inserted between the layers. Clearly, the bilayer NiN_2 effectively screens the repulsive Coulomb interaction between lithium atoms, resulting in small changes in the electronic properties of the bilayer NiN_2 during

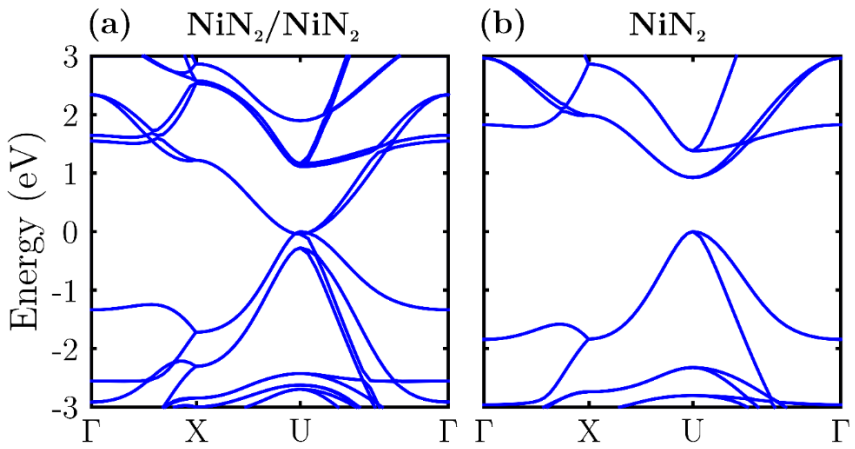

Figure S2. Electronic band structure of (a) bulk NiN_2 with two layers as the basic unit and (b) single-layer NiN_2 calculated by HSE06 hybrid functional. The top of the valence bands are set to 0 eV.

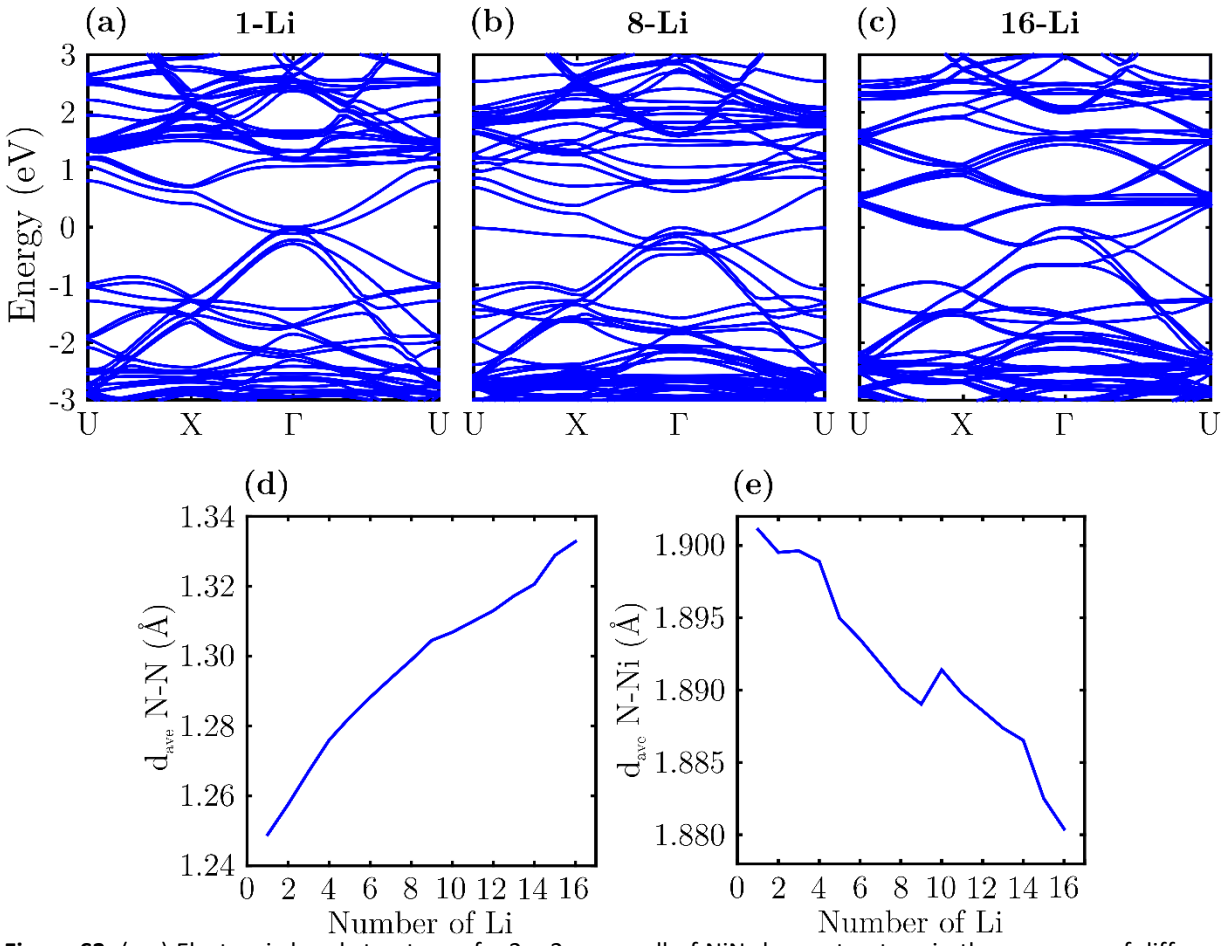

Figure S3. (a-c) Electronic band structure of a 2 × 2 supercell of NiN_2 homostructure in the presence of different lithium intercalation concentrations calculated by HSE06 hybrid functional. The top of the valence bands are set to 0 eV. Average interatomic distance variation for (d) N-N atoms and (e) N-Ni atoms.

the intercalation process. Furthermore, using the following formula, we calculated the average interatomic distance for N-N and N-Ni atoms in the system:

$$d_{ave} = \frac{1}{Q}\sum_{i,j}^{Q}\sqrt{(x_i - x_j)^2 + (y_i - y_j)^2 + (z_i - z_j)^2} \quad (1)$$

where, Q is the total number of atom pairs considered in the calculation, and x, y, and z are the positions of the atoms in different directions, respectively. As expected, under different lithium intercalation concentrations, the average interatomic distance for N-N atoms is more affected (Figure S3d) than that of N-Ni atoms (Figure S3e). Here, the average interatomic distance for N-N atoms increases from 1.2489 Å for 1-Li to 1.3328 Å for 16-Li; conversely, the average interatomic distance for N-Ni atoms displays a decreasing trend from 1.9011 Å for 1-Li to 1.8804 Å for 16-Li.

3. Thermodynamic and Electrostatic Potential Properties of G/NiN_2

To check the thermal stability of the graphene/NiN_2 (G/NiN_2) heterostructure, we performed the molecular dynamics (MD) simulation using the NVT canonical ensemble controlled by a Nosé thermostat at a temperature of 300 K [3]. During the MD simulation, the average fluctuation of the free energy was less than 0.0976 eV at an average temperature of 499.3756 K (Figure S4a). This result reveals that the G/NiN_2 heterostructure has good thermodynamic stability. Furthermore, the electrostatic potential of the G/NiN_2 heterostructure perpendicular to the surface is depicted in Figure S4b. One can see the profile is flat within the vacuum region, and there is a symmetric electrostatic potential behavior for the individual layer. Here, the balanced electrostatic potential can be interpreted as a stable interface between the layers, where minimal charge transfer occurs, contributing to the overall stability of the heterostructure.

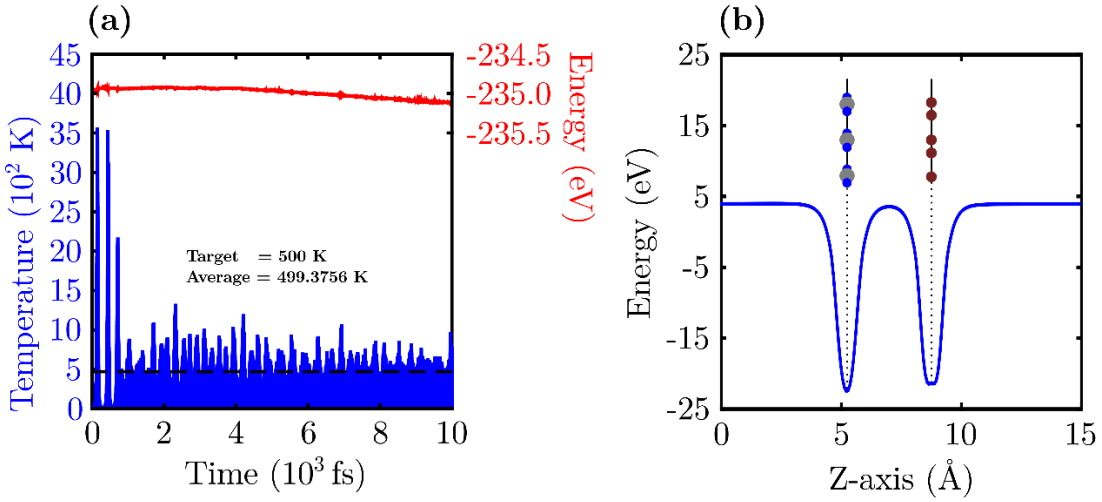

Figure S4. (a) Temperature and free energy as a function of MD time with 1fs step size, and (b) schematic profile of the electrostatic potential as a function of position for 2D G/NiN_2 heterostructure. Brown spheres represent C (= carbon) atoms.

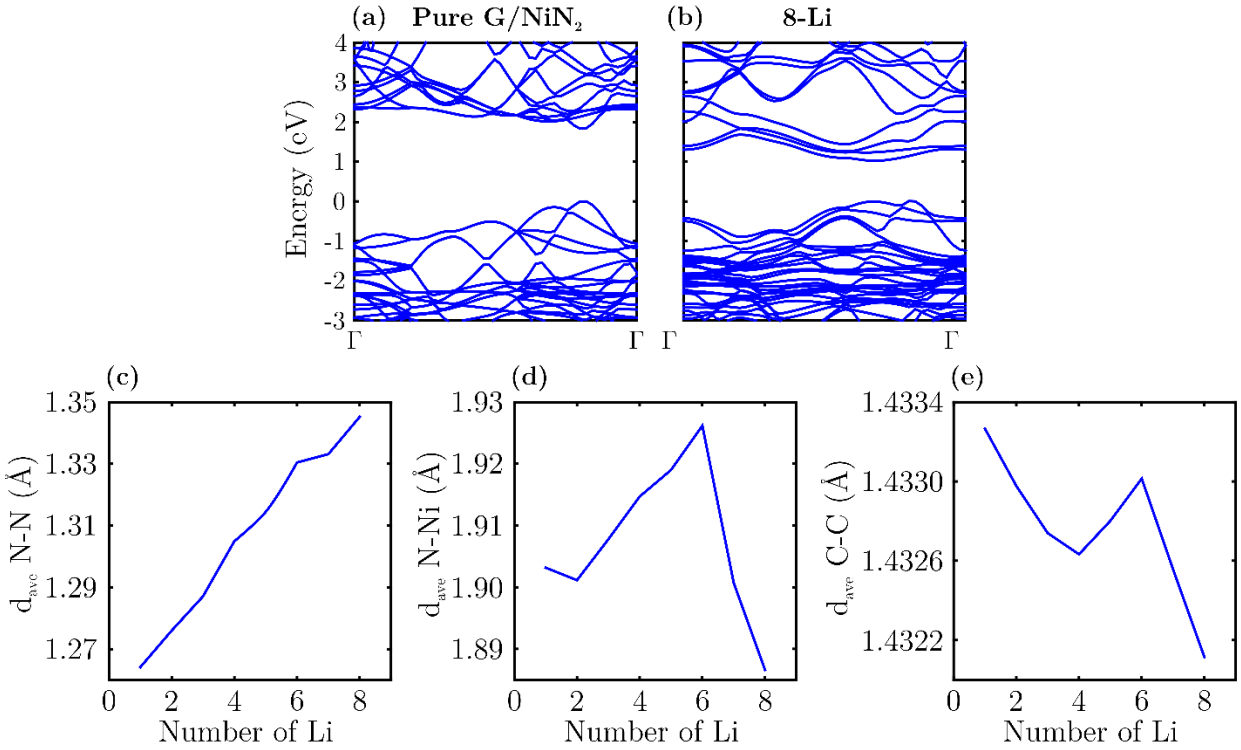

Figure S5. Electronic band structure of G/NiN_2 heterostructure (a) without and (b) with eight lithium atoms intercalation calculated by HSE06 hybrid functional. The top of the valence bands are set to 0 eV. Average interatomic distance variation for (c) N-N atoms, (d) N-Ni atoms, and (e) C-C atoms versus different lithium concentrations.

4. Electronic Band Structure of G/NiN_2 and ADA under Different Lithium Intercalation Concentrations

As shown in Figure S5a,b, the combination of single layers of graphene and NiN_2 results in a 2D van der Waals (vdW) semiconductor heterostructure. Here, to reduce the computational cost, we stacked the pre-strained structures of a graphene nanoribbon and a 2 × 1 supercell of single-layer NiN_2, ensuring a suitable lattice mismatch without disturbing the characterization of the two materials. The lattice constants of the G/NiN_2 heterostructure are a = 8.84972 Å and b = 4.75547 Å, and the average lattice mismatches are 3.405% and 3.789% in the X and Y directions, respectively. Clearly, when the lithium atoms are uniformly distributed in the interlayer region of the bilayer, the band structure exhibits a smoother behavior. In this case, the average interatomic distance for N-N atoms (Figure S5c) increases from 1.2641 Å for 1-Li to 1.3452 Å for 8-Li, which can be attributed to a strain ranging from 1.76% to 8.29%. On the other hand, the average interatomic distance for N-Ni atoms (Figure S5d) fluctuates between 1.9031 Å and 1.8865 Å during the lithium intercalation process, corresponding to a strain variation of less than 0.8%. In addition, this value for C-C atoms (Figure S5e) shifts from 1.4332 Å for 1-Li to 1.4321 Å for 8-Li, which indicates a strain variation of less than 0.6%.

5. Energy of the System

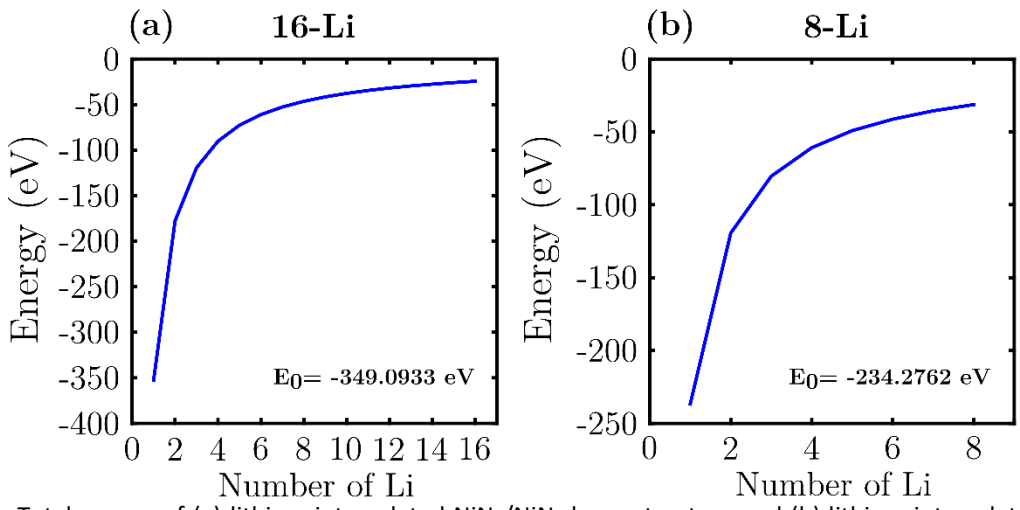

Figure S6. Total energy of (a) lithium-intercalated NiN_2/NiN_2 homostructure and (b) lithium-intercalated G/NiN_2 heterostructure per injected atom under different concentrations. E_0 represents the energy of systems before intercalation.

6. References

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