Supporting Information

Nitrogen fixation on metal-free SiC(111) polar surfaces

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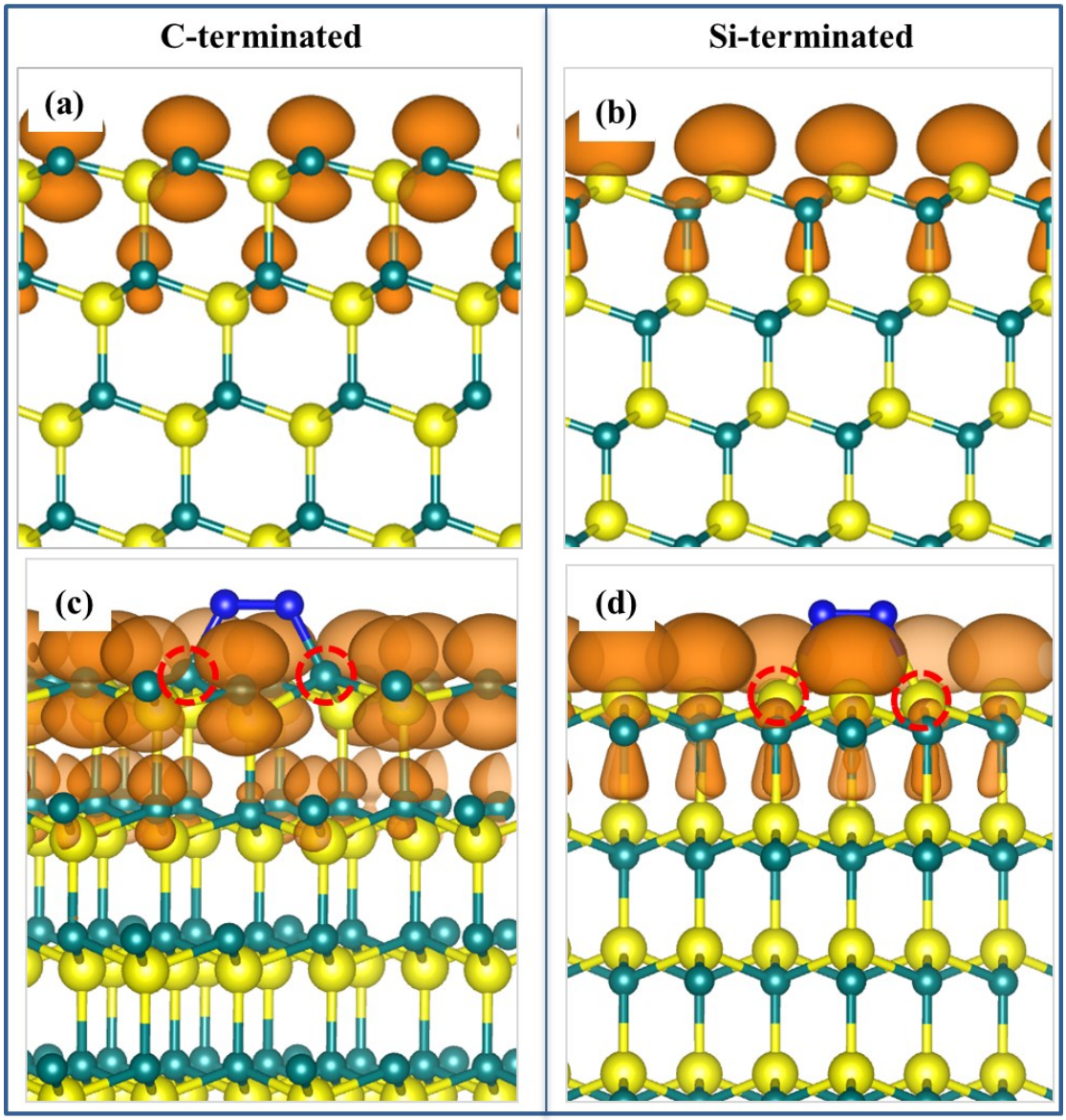

Fig. S1 The spin density of the (a) C- and (b) Si-terminated SiC(111) surfaces as well as N_2 adsorption *vis* side-on configurations on (c) C- and (d) Si-terminated SiC(111) surfaces, in which the isosurface value is set to be 0.006 e/Å^3.

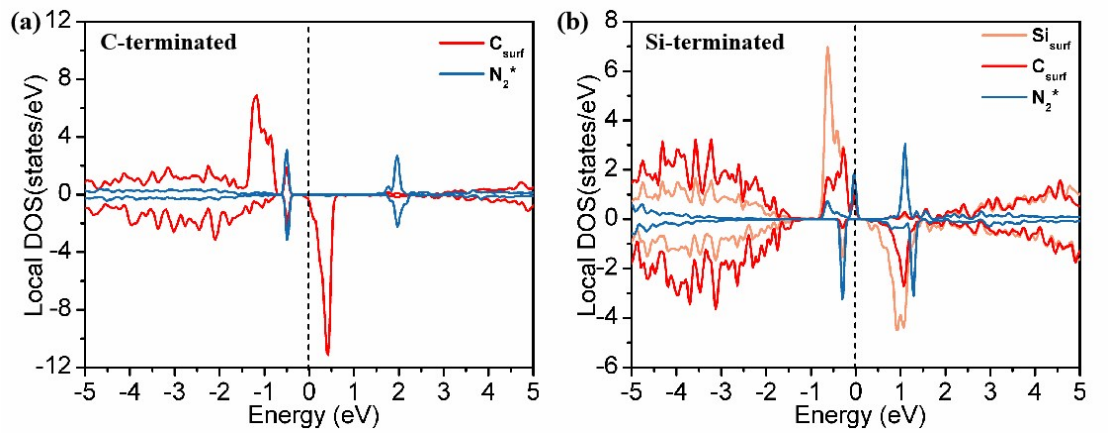

Fig. S2 The LDOS of the (a) C- and (b) Si-terminated SiC(111) surface after N_2 adsorption by side-on pattern. The Fermi level was set to be zero as denoted by the black dashed line.

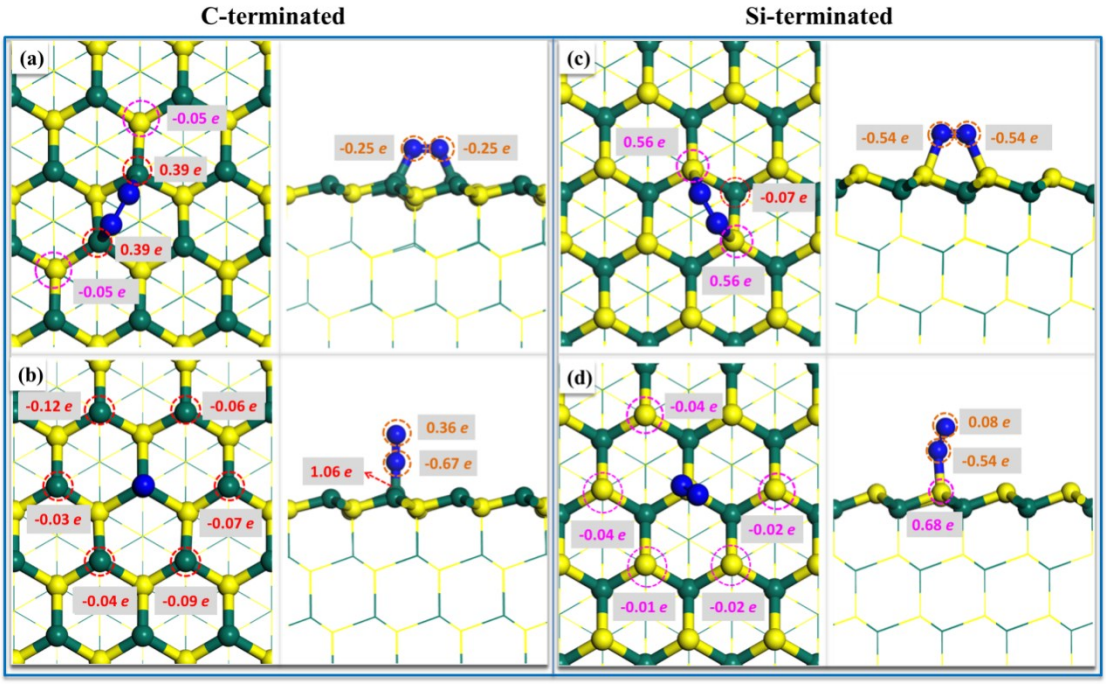

Fig. S3 The Bader charge changes of the (a-b) C- and (c-d) Si-terminated SiC(111) surface atoms before and after adsorption of N_2. Positive and negative values indicate the loss or gain of electrons, respectively.

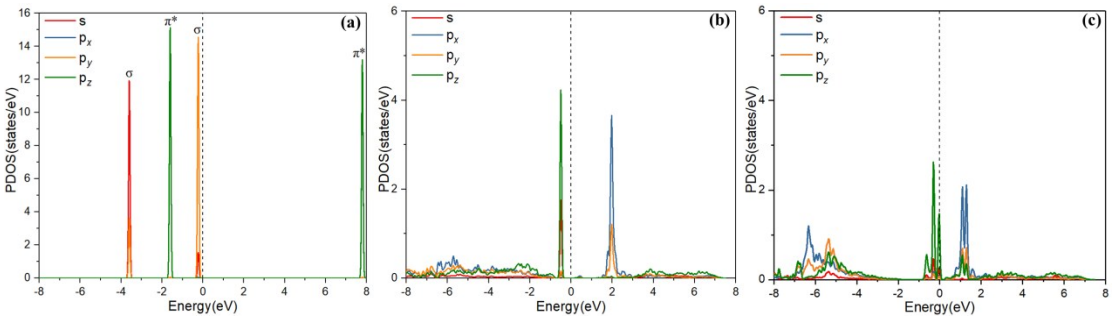

Fig. S4 The partial density of states (PDOS) of (a) free N_2 and N_2 adsorbed by side-on pattern on the (b) C- and (c) Si-terminated SiC(111) surfaces.

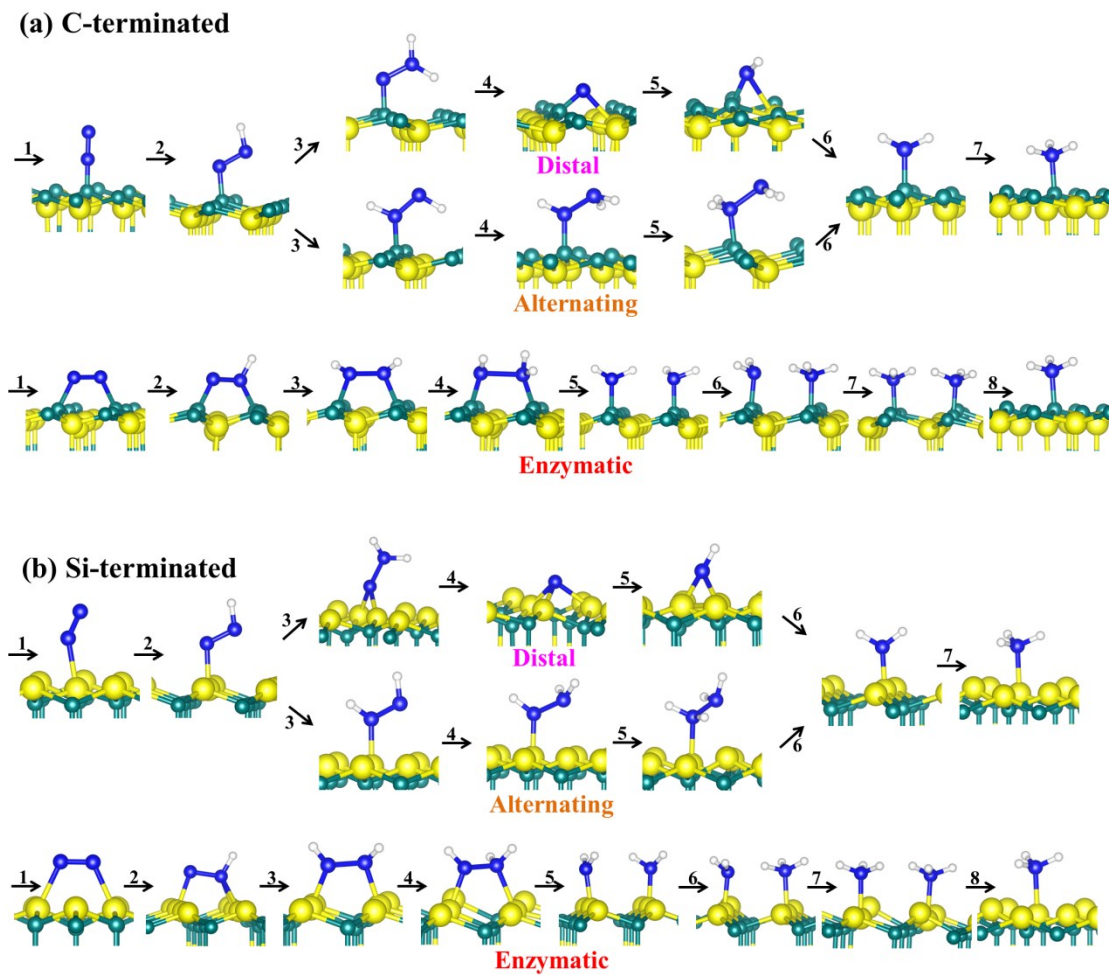

Fig. S5 Optimized structures of various intermediates along the reaction paths of the NRR proceeding on the (a) C- and (b) Si-terminated SiC (111) surfaces through distal, alternating and enzymatic pathways.

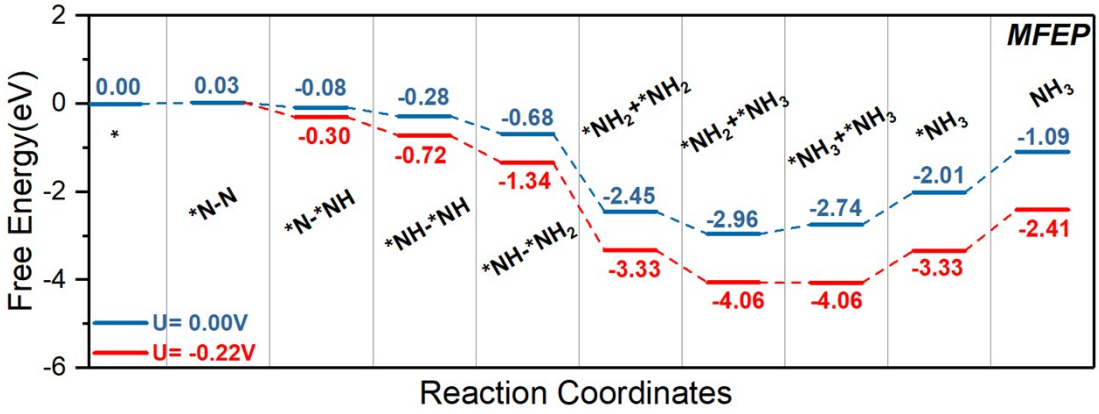

Fig. S6 The free energy diagrams for N_2 reduction on the C-terminated SiC (111) surface through a minimum free energy pathway (MFEP) at different applied potentials.

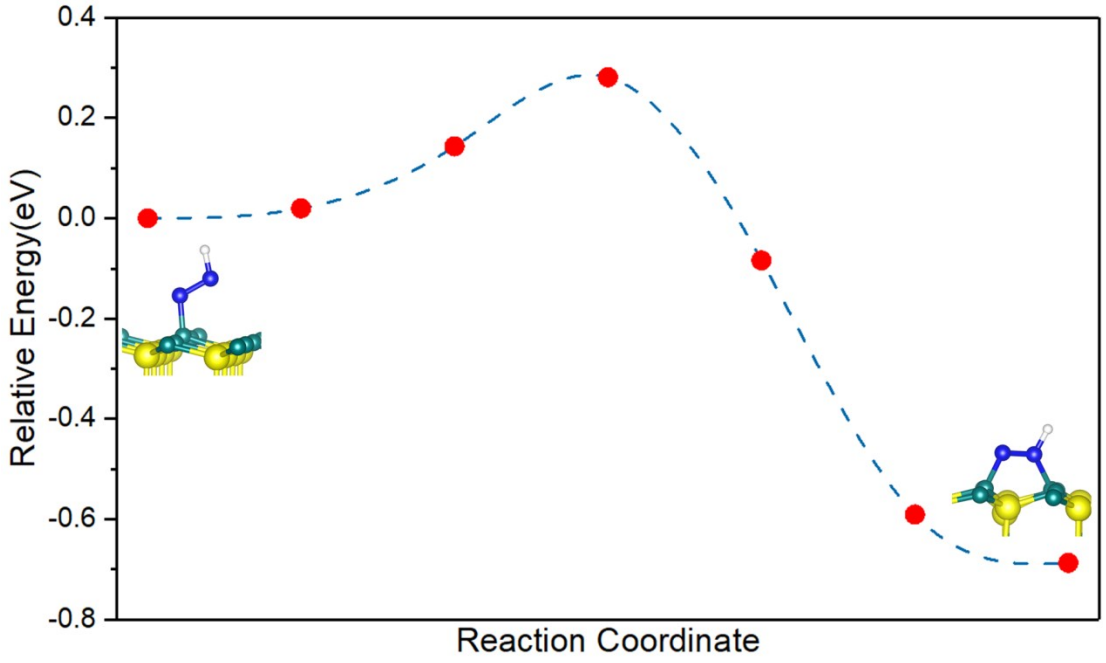

Fig. S7 The minimum reaction pathway for $*N_2H$ species from the end-on configuration to the side-on configuration on the C-terminated SiC (111) surface with a barrier of 0.28 eV.

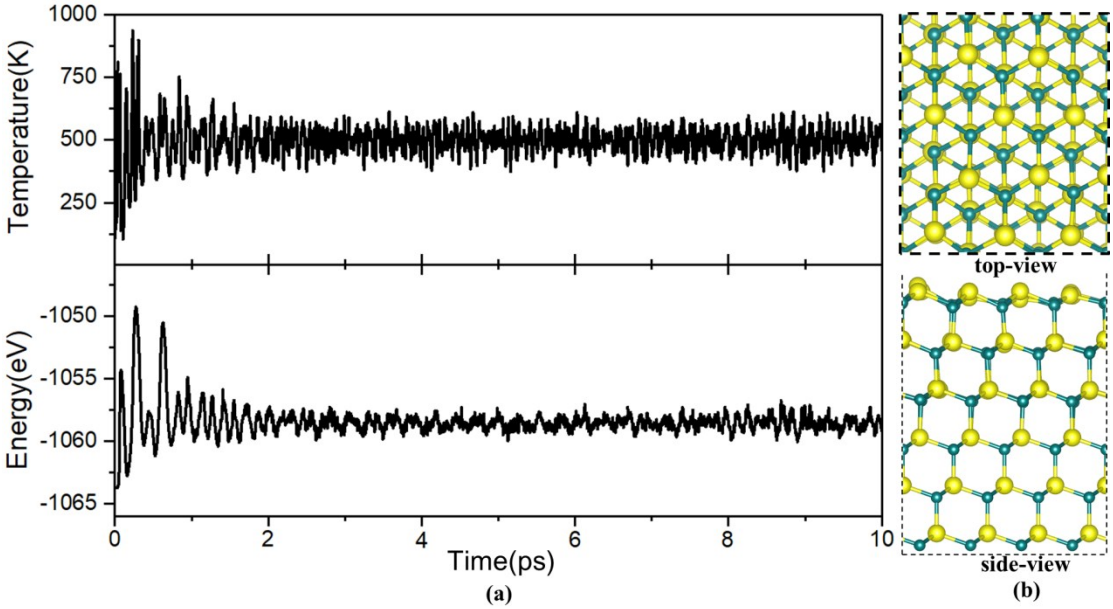

Fig. S8 (a) Variations of temperature and energy against the time for AIMD simulations of the Si-terminated SiC(111) surface; the simulation is run under 500 K for 10 ps with a time step of 2 fs. (b) The structure of the Si-terminated surface after dynamics simulation.

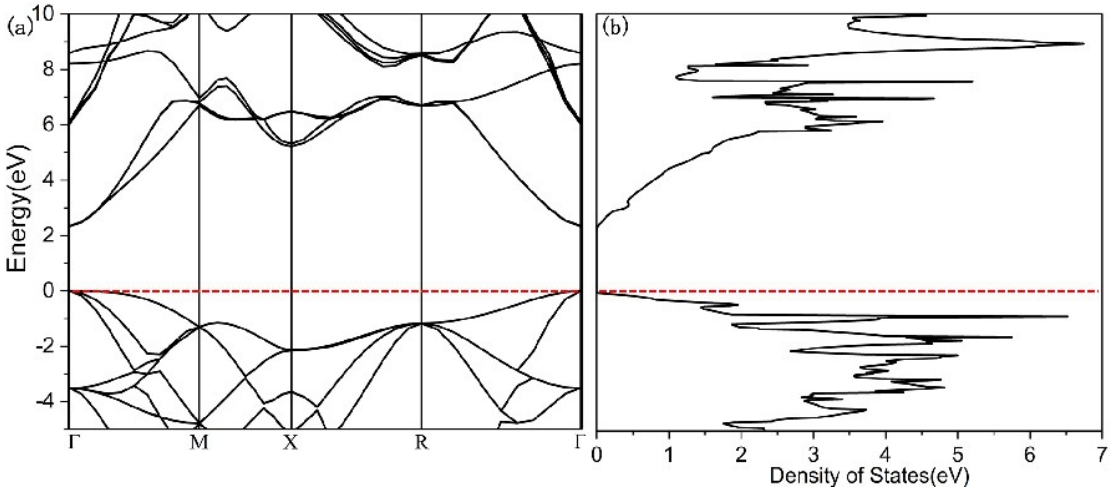

Fig. S9 (a) Band structure and (b) DOS of bulk SiC calculated by HSE06 functional with bandgap of 2.34 eV. Fermi levels are set to zero and represented by red dash lines.