Supporting Information for

Electrocatalytic Dinitrogen Reduction Reaction on Silicon Carbide: a Density Functional Theory Study

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Abstract: Approaches that advance electrochemical nitrogen fixation under ambient conditions and powered by renewable energy are challenged by the identification of an effective electrocatalysts for nitrogen reduction. Silicon carbide is investigated computationally as a metal-free, surface-derived catalyst for the electrocatalytic nitrogen reduction reaction. As demonstrated by first-principle calculations, Si-terminated and C-terminated surfaces with the Si and C as active sites are all reactive for dinitrogen capture and activation, resembling the catalytic behaviour of popular B-based electrocatalysts, but the latter (C-terminated) offers an ultralow over-potential of 0.39 eV, being lower than most metals and alloys, while retarding hydrogen evolution. This research enriches the design of catalysts for dinitrogen fixation under ambient conditions, meanwhile indicates a new direction of Si-based materials for nitrogen reduction.

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1. Partial density of states of *NN on SiC

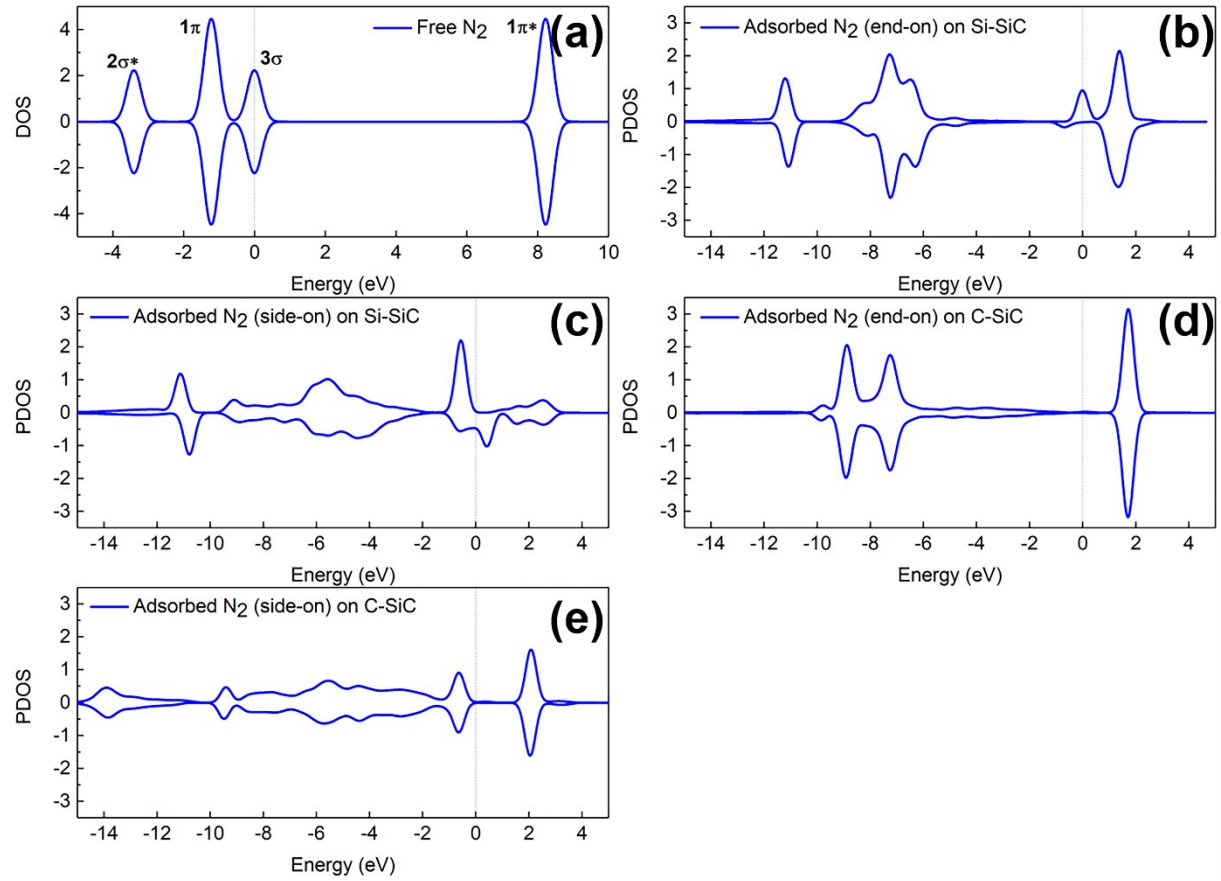

Figure S1. PDOS of free nitrogen molecule (a) and adsorbed dinitrogen adatoms on Si-SiC (b, c) and C-SiC (d, e).

2. Charge analyses

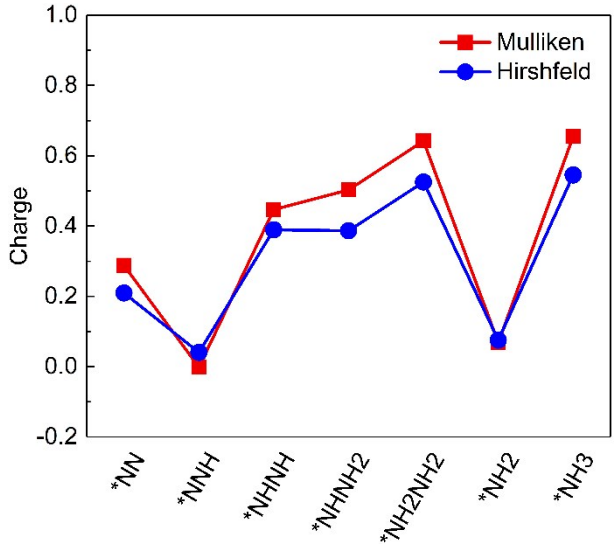

Figure S2. Mulliken and Hirshfeld charge analyses for reaction intermediates on C-SiC along the alternating reaction pathway.

3. N-N bond evolution

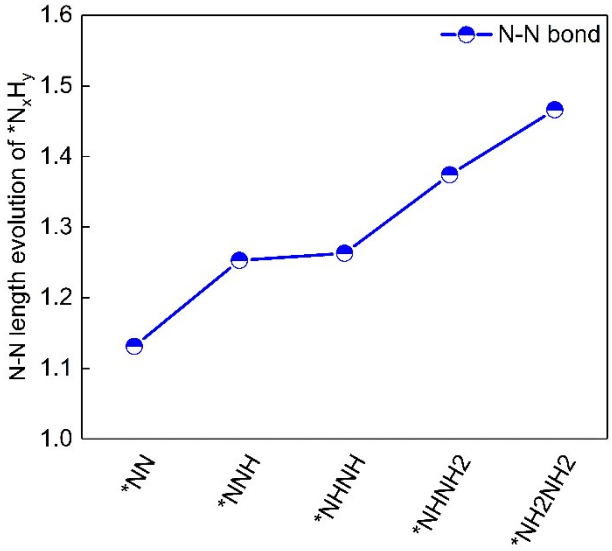

Figure S3. The length changes of N-N bond along the alternating reaction pathway on C-SiC.

4. Comparison with some recently reported results

Table S1. Recent reports for ENRR in comparison with our calculations on SiC

Catalyst materials	Results		References
	Experiments	Theoretical calculations	
Boron-doped InSe monolayer	—	η = 0.50 V (U_L = -0.66 V, distal pathway)	**1**
Mo-Phthalocyanine monolayer	—	η = 0.54 V (U_L = -0.70 V, distal/alternating pathway)	**2**
Ni-WS_2 (single Nil atom supported on defective WS2 monolayer)	—	η = 0.70 V (U_L = -0.86 V, distal/alternating pathway)	**3**
Bioinspired Fe_3C@C composite	r(NH_3) = 8.53 μg h^{-1} mg^{-1} at -0.2 V vs. RHE, FE = 9.15%	η = 0.667 V (U_L = -0.827 V, alternating pathway)	**4**
Ru single-atom on PtS_2	—	η = 0.93 V (U_L = -1.09 V, distal pathway)	**5**
Ru doped Mo_2CTx MXene	r(NH_3) = 40.57 μg h^{-1} mg^{-1} at -0.3 V vs. RHE, FE =	η = 0.80 V (U_L = -0.96 V, distal pathway)	**6**

	25.77%		
Ti@VB_2 (single-atom doped on 2D metal diborides)	–	η = 0.45 V (U_L = -0.61 V, distal/alternating pathway)	**7**
Mo-doping in MnO_2 nanoflowers	r(NH_3) = 36.6 μg h^{-1} mg^{-1} at -0.5 V vs. RHE, FE = 12.1% at -0.4 V	η = 0.79 V (U_L = -0.95 V, distal pathway)	**8**
SiC	**–**	**η = 0.39 V (U_L = -0.55 V, alternating pathway)**	**This work**

5. Free energy correction of NRR on Si-SiC

Table S2. Gibbs free energy of reaction intermediates on Si-SiC.

Intermediates	DFT energy/E_{DFT}	Gibbs free energy/G
*(Si-SiC)	-401207.71	-401207.71
*NN (end-on)	-404189.53	-404189.37
*NN (side-on)	-404190.02	-404189.86
*NNH	-404207.18	-404206.72
*NNH_2	-404222.31	-404221.55
*N	-402699.79	-402699.71
*NH	-402716.30	-402715.92
*NH_2	-402733.44	-402732.76
*NH_3	-402749.22	-402748.24
*NHNH	-404223.97	-404223.21
*$NHNH_2$	-404238.69	-404237.63
*NH_2NH_2	-404255.27	-404253.91

6. Free energy correction of NRR on C-SiC

Table S3. Gibbs free energy of reaction intermediates on C-SiC.

Intermediates	DFT energy/E_{DFT}	Gibbs free energy/G
*(C-SiC)	-401206.84	-401206.84
*NN (end-on)	-404188.96	-404188.80
*NN (side-on)	-404188.66	-404188.50
*NNH	-404204.76	-404204.30
*NNH_2	-404221.43	-404220.67
*N	-402696.38	-402696.30
*NH	-402713.77	-402713.39
*NH_2	-402731.58	-402730.90
*NH_3	-402748.76	-402747.78
*NHNH	-404221.55	-404220.79
*$NHNH_2$	-404238.10	-404237.04
*NH_2NH_2	-404254.94	-404253.58

7. References

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