Supporting Information

Single boron modulated Graphdiyne nanosheet for efficient electrochemical nitrogen fixation: A First-Principles Study

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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

1. Table S1. The calculated N_2 adsorption energies for B@GDY configurations via end-on and side-on mode, together with bond lengths and Bader charge values of catalytic models.

2. Fig. S1. The cohesive energies of pristine GDY and single boron atom doped B@GDY configurations.

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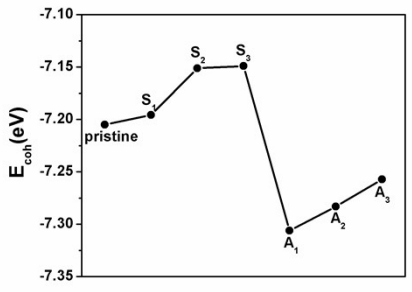
6. Fig. S5. (a) Free energy diagram for the HER on B(S_3)@GDY and (b) the corresponding structures of B(S_3)@GDY with H atom adsorbed after optimization.

7. Fig. S6. Partial density of states (PDOS) of N_2 molecule adsorbed on B(S_2)@GDY and the Fermi level is set to zero, as shown by the black dashed line.

Table S1. The calculated N_2 adsorption energies for B@GDY configurations via end-on and side-on mode, together with bond lengths and Bader charge values of catalytic models.

Configuration		Adsorption energy (E_{ads}/eV)	Bond length (Å)		Bader charge value (q/*e*)			
					B atom		N atom	
			N–N	B–N	before N_2 fixtion	after N_2 fixtion	proximal	distal
B(S_2)@GDY	end-on	–0.12	1.13	1.48	1.83	1.86	–0.56	0.19
B(S_3)@GDY	end-on	–0.08	1.13	1.50	1.85	1.90	–0.54	0.23
	side-on	1.79	1.20	1.61	1.85	1.82	–0.22/0.01	
B(A_1)@GDY	end-on	0.29	1.13	1.53	1.56	1.60	–0.54	0.27
	side-on	0.89	1.22	1.55/1.56	1.56	1.77	–0.48/–0.40	
B(A_2)@GDY	end-on	–1.22	1.16	1.38	1.19	1.73	–0.86	0.20
	side-on	–0.12	1.21	1.57/1.64	1.19	1.78	–0.50/–0.37	
B(A_3)@GDY	end-on	–0.96	1.16	1.39	1.08	1.82	–0.83	0.15
	side-on	–0.31	1.22	1.55/1.56	1.08	1.87	–0.42/–0.29	



Configuration	pristine GDY	B(S_1)@GDY	B(S_2)@GDY	B(S_3)@GDY	B(A_1)@GDY	B(A_2)@GDY	B(A_3)@GDY
E_{coh}(eV)	–7.205	–7.196	–7.151	–7.149	–7.306	–7.283	–7.257

Fig. S1. The cohesive energies of pristine GDY and single boron atom doped B@GDY configurations.

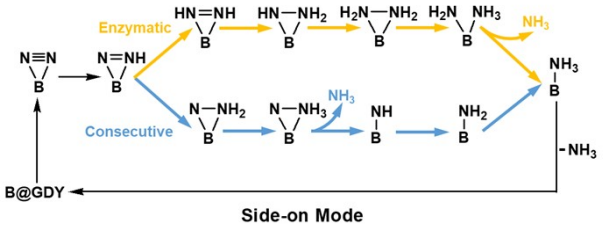


Fig. S2. Schematic depiction of the enzymatic and consecutive pathways for N_2 reduction via side-on mode of N_2 adsorption.

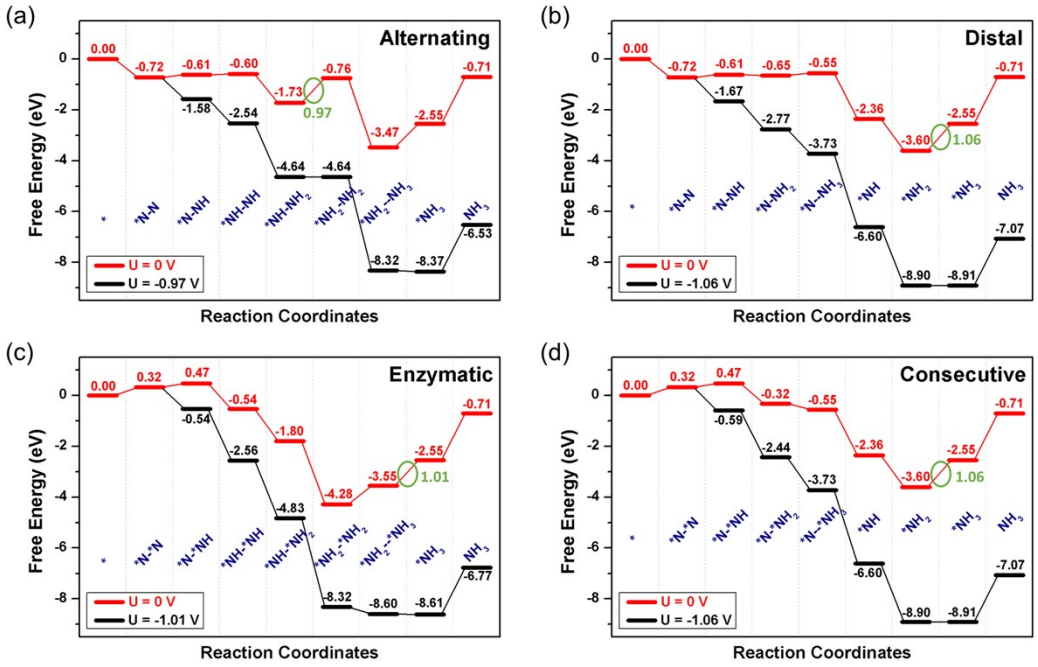


Fig. S3. Potential energy surfaces for NRR on B(A_2)@GDY configuration through (a) alternating, (b) distal mechanisms at different applied potentials, together with free energy and (c) the relative geometric structures for each elementary step.

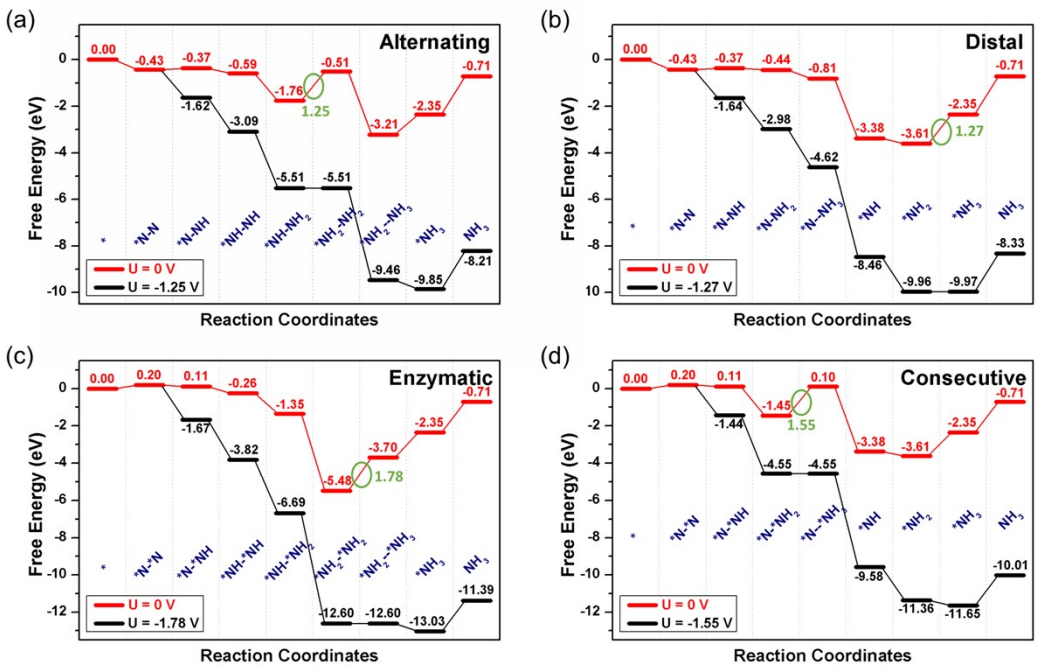
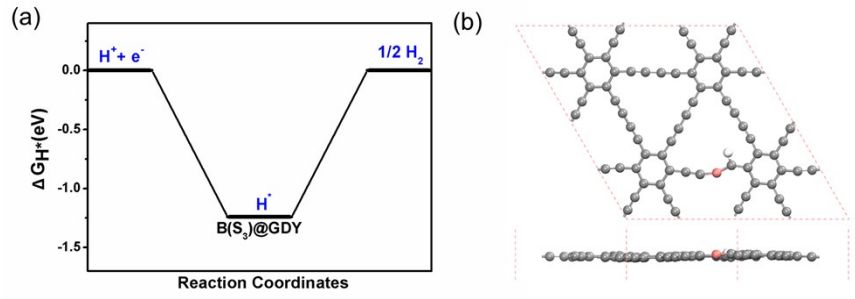


Fig. S4. Potential energy surfaces for NRR on B(A_3)@GDY configuration through (a) alternating, (b) distal mechanisms at different applied potentials, together with free energy and (c) the relative geometric structures for each elementary step.



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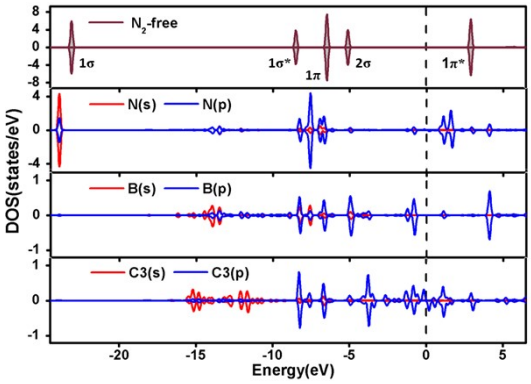

Fig. S6. Partial density of states (PDOS) of N_2 molecule adsorbed on $B(S_2)$@GDY and the Fermi level is set to zero, as shown by the black dashed line.