Supplementary Information

Electrocatalytic nitrogen reduction directed through the p-band center of boron on $B_{SAC}@Mo_2C$

Ashakiran Maibam,[ab] Sailaja Krishnamurty[ab]* and Manzoor Ahmad Dar[c]*

a *Physical and Materials Division, CSIR-National Chemical Laboratory, Pune 411 008, India*

b *Academy of Scientific and Innovative Research, CSIR-Human Resource Development Centre (CSIR-HRDC) Campus, Postal Staff College area, Gaziabad, 201002, Uttar Pradesh, India*

c *Department of Chemistry, Islamic University of Science and Technology, Awantipora, Jammu and Kashmir 192122, India*

Email: sailaja.raaj@gmail.com, manzoor.dar@islamicuniversity.edu.in;

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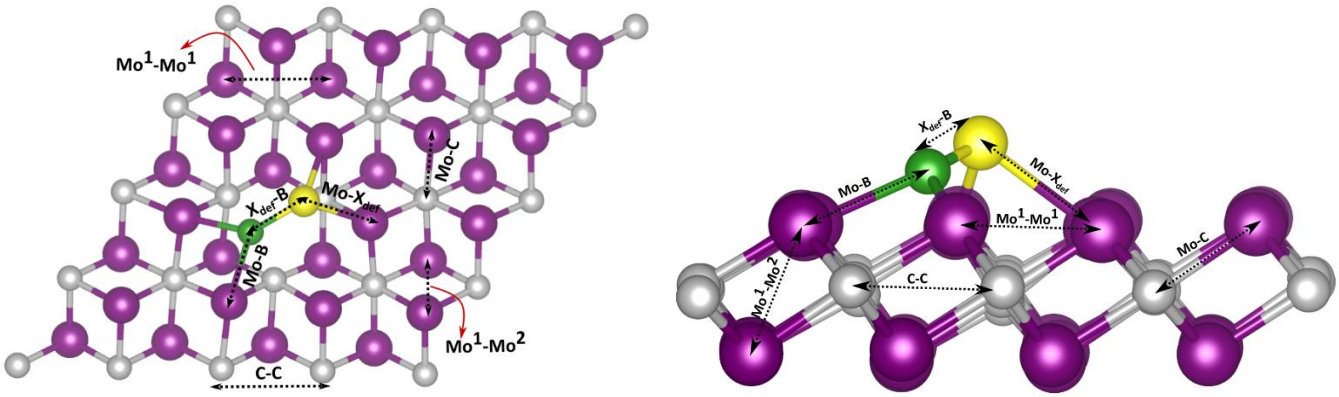
Table S1. Binding energy of B on Mo_2C substrates, B p-band center, Mo d-band center and Bader charges on the B atom.

B_{cat}@Mo_2C	**Binding energy (per boron atom) in eV**	**B p-band center (eV)**	**Mo d-band center (eV)**	**Bader charge on B**
B_{SAC}@Mo_2C	-6.90	-1.19	-1.19	-0.58
B_{DAC}@Mo_2C	-7.07	-1.50	-1.16	-0.43, -0.49
B_{SAC}@Mo_2C-Mo_{vac}	-5.35	-0.75	-1.30	-0.41
B_{SAC}@Mo_2C-B_{def}	-6.25	-1.25	-1.26	-0.47, 0.91 (B_{def})
B_{SAC}@Mo_2C-C_{def}	-5.36	-0.75	-1.29	-0.37
B_{SAC}@Mo_2C-N_{def}	-7.92	-2.61	-1.30	0.67
B_{SAC}@Mo_2C-P_{def}	-5.81	-1.46	-1.28	-0.35
B_{SAC}@Mo_2C-S_{def}	-4.77	-1.49	-1.27	-0.07



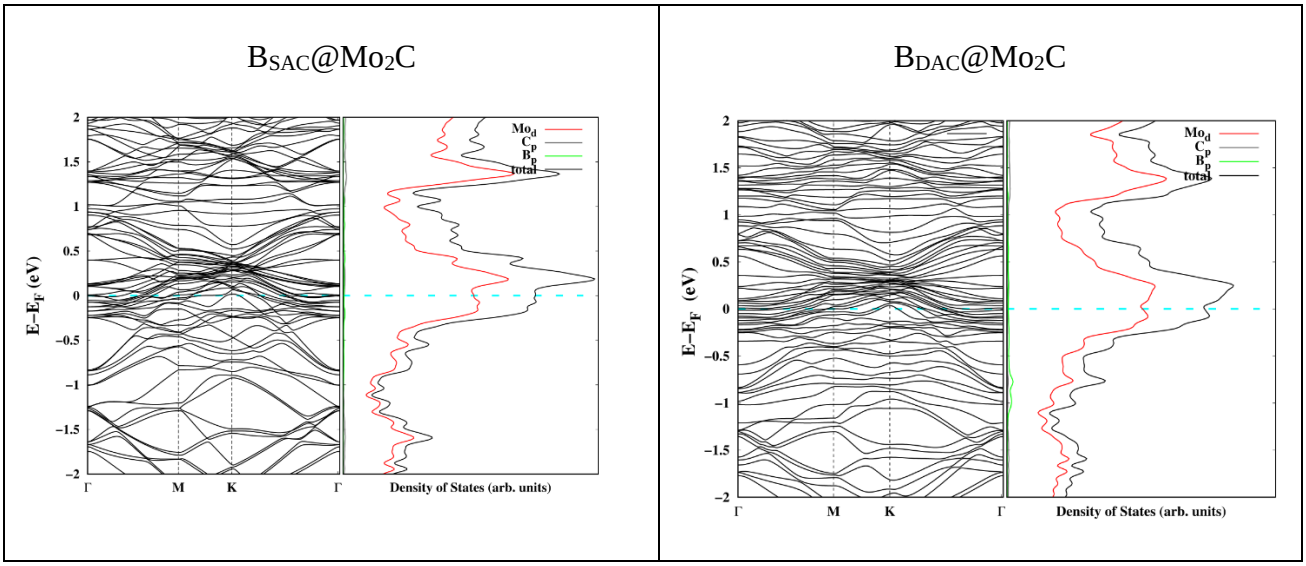
(a) Top view of B_{cat}@Mo_2C (b) Side view of B_{cat}@Mo_2C

Figure S1: Top and side view of a B_{cat}@Mo_2C structure showing all the essential bonds; Mo^1-Mo^1 is the distance between two Mo atoms on the same layer while Mo^1-Mo^2 is the distance between two Mo atoms on different layers.

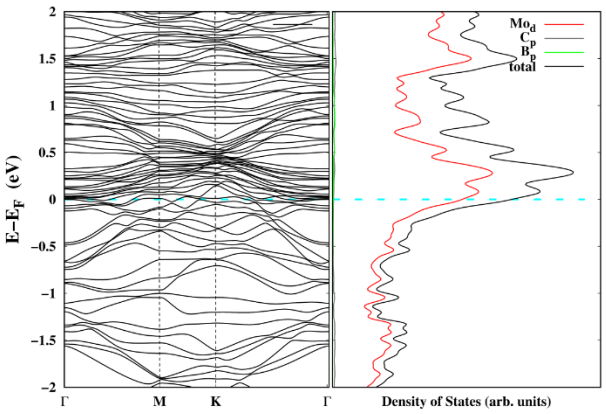
Table S2: Bond lengths in Angstroms (Å), e.g. Mo-Mo$_{avg}$, Mo-C$_{avg}$, C-C$_{avg}$, B-X$_{def}$, Mo-B distances in the optimized structures.

	Mo^1-Mo$^1_{avg}$	**Mo^1-Mo$^2_{avg}$**	**Mo-C$_{avg}$**	**C-C$_{avg}$**	**Mo-B**	**X$_{def}$-B**	**Mo-X$_{def}$**
B$_{SAC}$@Mo$_2$C	3.08	2.84	2.10	3.05	2.13		
B$_{DAC}$@Mo$_2$C	3.10	2.85	2.10	3.08	2.23	B-B (1.66)	
B$_{SAC}$@Mo$_2$C-Mo$_{vac}$	3.09	2.85	2.09	3.05	2.08		
B$_{SAC}$@Mo$_2$C-B$_{def}$	3.00	2.80	2.10	3.10	2.20	1.82	2.38
B$_{SAC}$@Mo$_2$C-C$_{def}$	3.10	2.80	2.09	3.10	2.18	1.55	2.38
B$_{SAC}$@Mo$_2$C-N$_{def}$	3.11	2.80	2.10	3.10	2.20	1.36	2.06
B$_{SAC}$@Mo$_2$C-P$_{def}$	3.00	2.80	2.10	3.10	2.40	1.85	2.54
B$_{SAC}$@Mo$_2$C-S$_{def}$	3.20	2.82	2.09	3.10	2.29	1.89	2.57

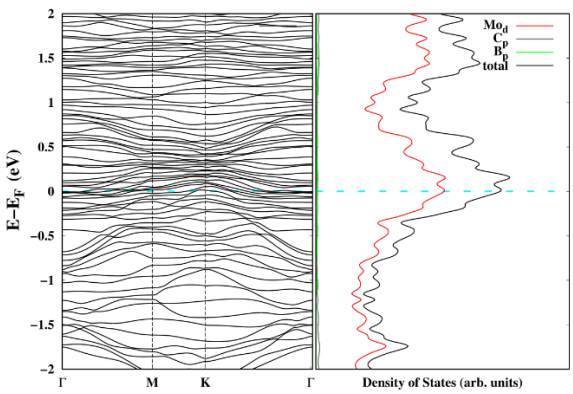
Table S3. Band diagram and Density of states plot of all B$_{cat}$@Mo$_2$C substrates



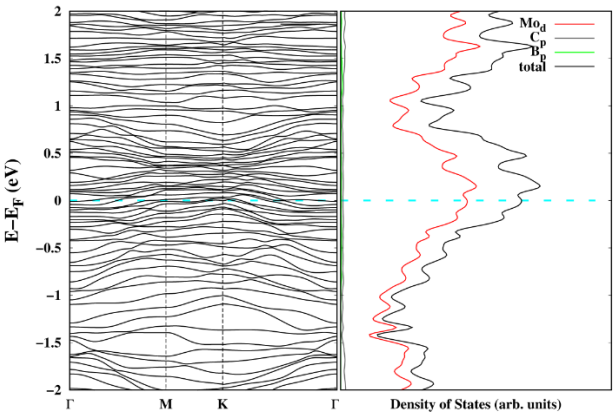
$B_{SAC}@Mo_2C\text{-}Mo_{vac}$



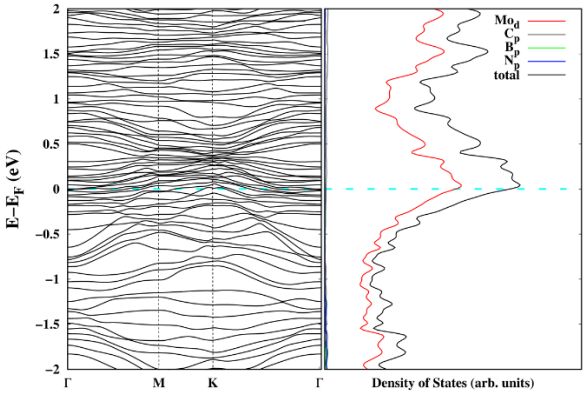
$B_{SAC}@Mo_2C\text{-}B_{def}$



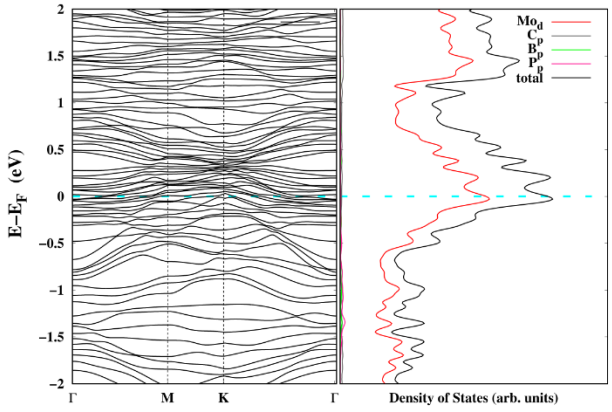
$B_{SAC}@Mo_2C\text{-}C_{def}$



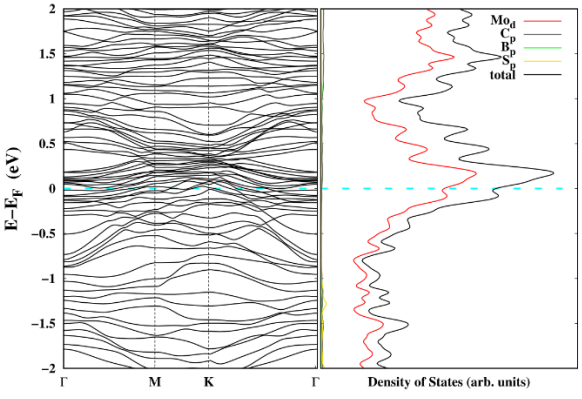
$B_{SAC}@Mo_2C\text{-}N_{def}$

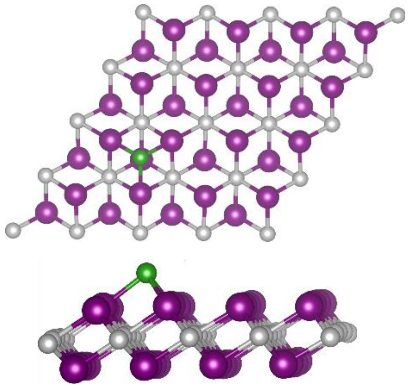


$B_{SAC}@Mo_2C\text{-}P_{def}$

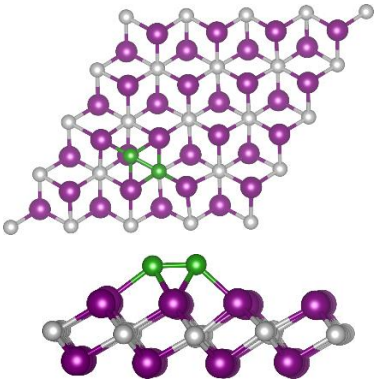


$B_{SAC}@Mo_2C\text{-}S_{def}$

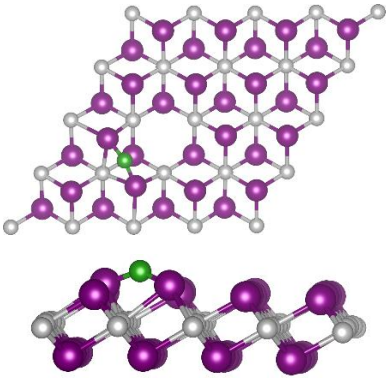




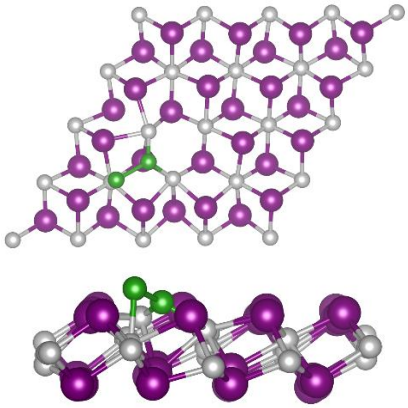
(a) Top-view and side-view of $B_{SAC}@Mo_2C$



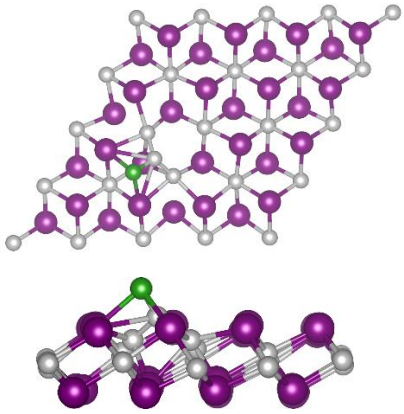
(b) Top-view and side-view of $B_{DAC}@Mo_2C$



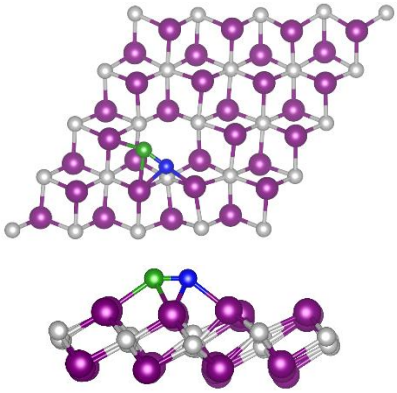
(c) Top-view and side-view of $B_{SAC}@Mo_2C\text{-}Mo_{vac}$



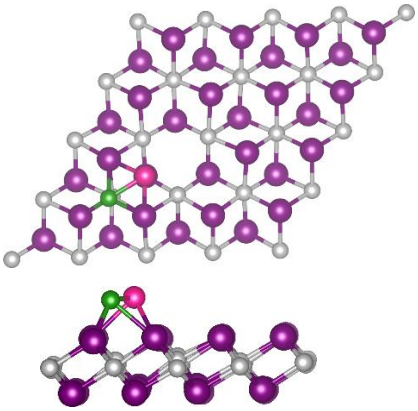
(d) Top-view and side-view of $B_{SAC}@Mo_2C\text{-}B_{def}$



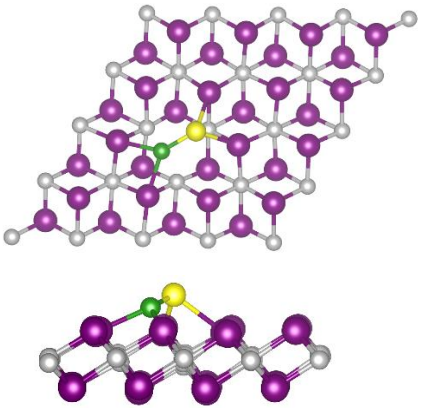
(e) Top-view and side-view of $B_{SAC}@Mo_2C\text{-}C_{def}$



(f) Top-view and side-view of $B_{SAC}@Mo_2C\text{-}N_{def}$

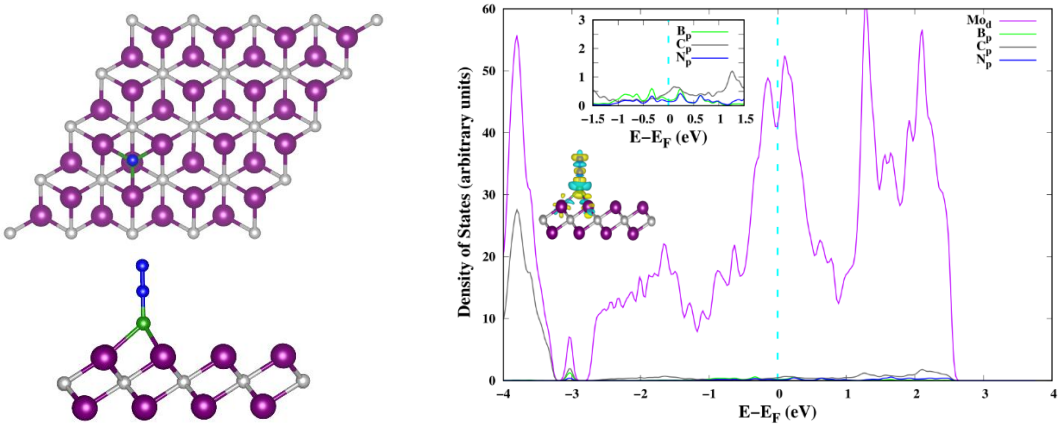


(g) Top-view and side-view of $B_{SAC}@Mo_2C\text{-}P_{def}$

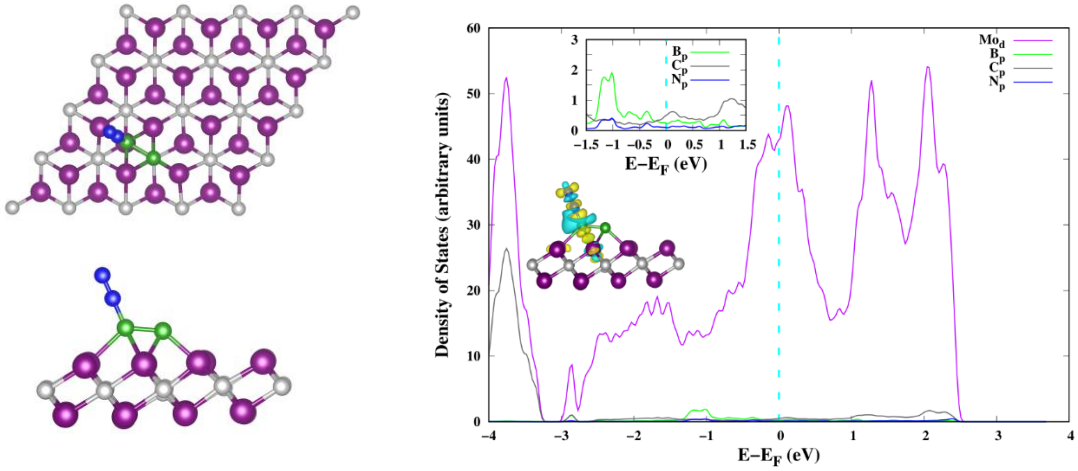


(h) Top-view and side-view of $B_{SAC}@Mo_2C\text{-}S_{def}$

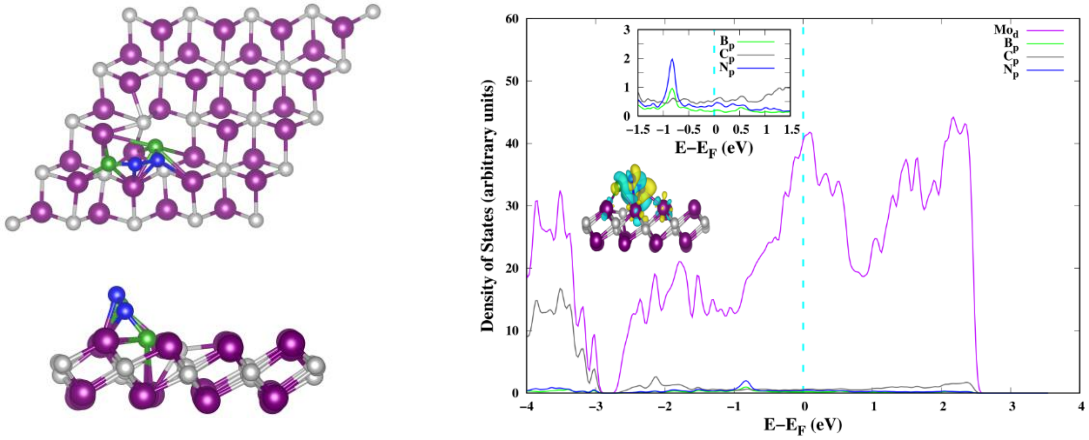
Figure S2: Geometric structure of all the $B_{cat}@Mo_2C$ catalysts considered in this study. Atomic colour code: C (grey), Mo (purple), B (green), N (blue), P (pink) and S (yellow).



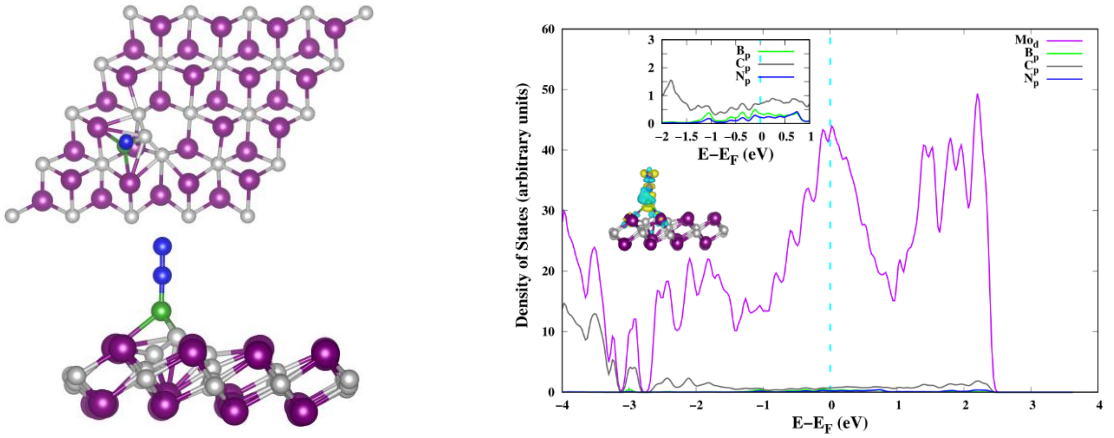
(a) Top-view and side view of N_2 adsorbed via end-on mode on B_{SAC}@Mo_2C along with its PDOS and CDD plots.



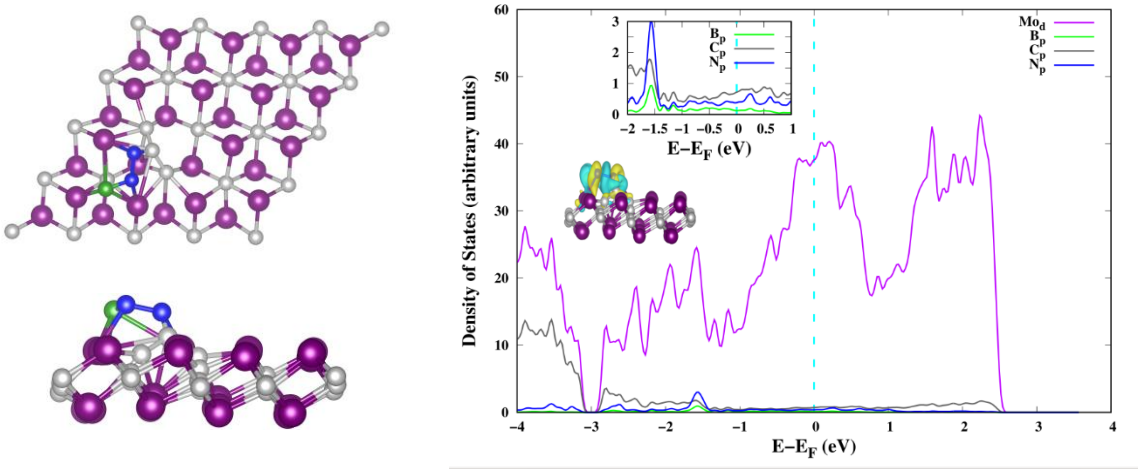
(b) Top-view and side view of N_2 adsorbed via end-on mode on B_{DAC}@Mo_2C along with its PDOS and CDD plots.



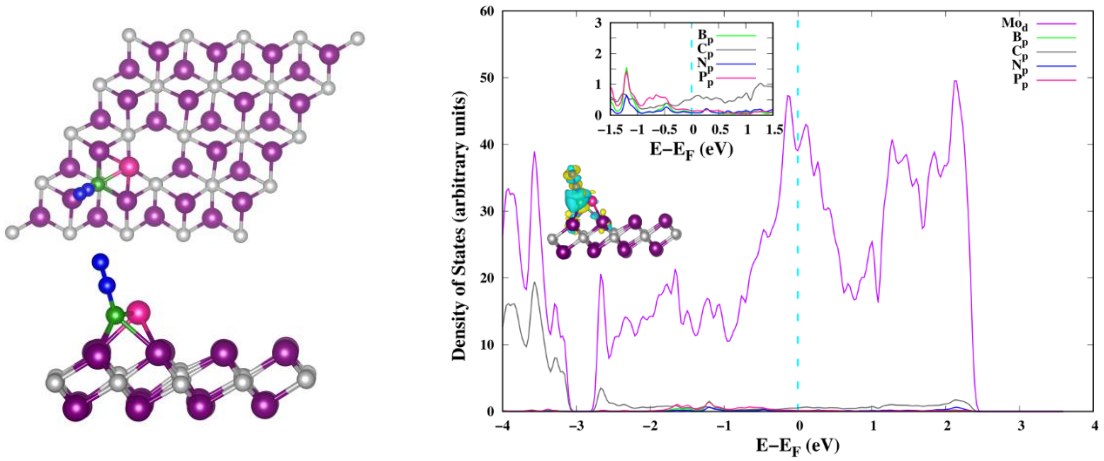
(c) Top-view and side view of N_2 adsorbed via side-on mode on B_{SAC}@Mo_2C-B_{def} along with its PDOS and CDD plots.



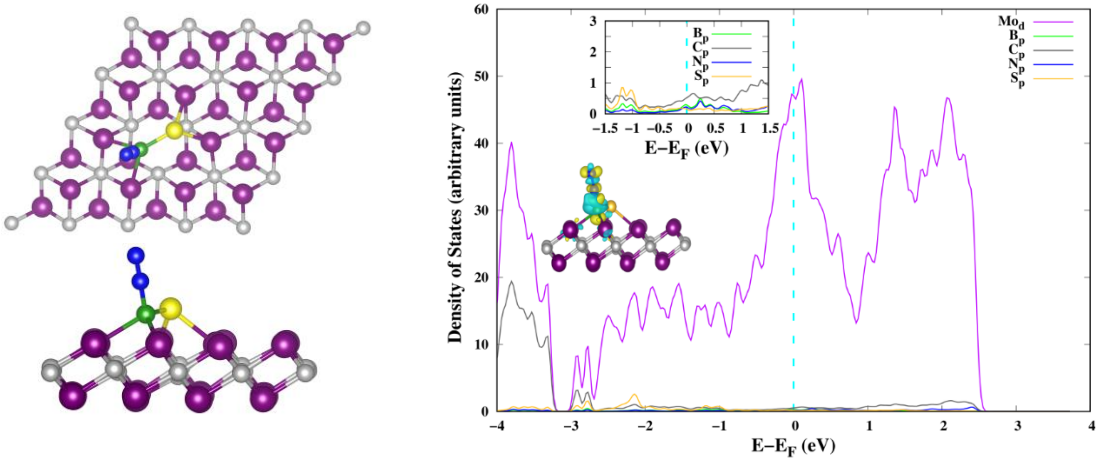
(d) Top-view and side view of N_2 adsorbed via end-on mode on B_{SAC}@Mo_2C-C_{def} along with its PDOS and CDD plots.



(e) Top-view and side view of N_2 adsorbed via side-on mode on B_{SAC}@Mo_2C-C_{def} along with its PDOS and CDD plots.



(f) Top-view and side view of N_2 adsorbed via end-on mode on B_{SAC}@Mo_2C-P_{def} along with its PDOS and CDD plots.



(g) Top-view and side view of N_2 adsorbed via end-on mode on B_{SAC}@Mo_2C-S_{def} along with its PDOS and CDD plots.

Figure S3: N_2 adsorbed geometries and Projected Density of States (PDOS) plots of N_2 adsorbed exothermally on all B_{cat}@Mo_2C substrates with insets showing the hybridisation of N p-orbitals and B p-orbitals and Charge Density Difference (CDD) plots generated at isosurface density set to 0.003 e/Å^{-3}.

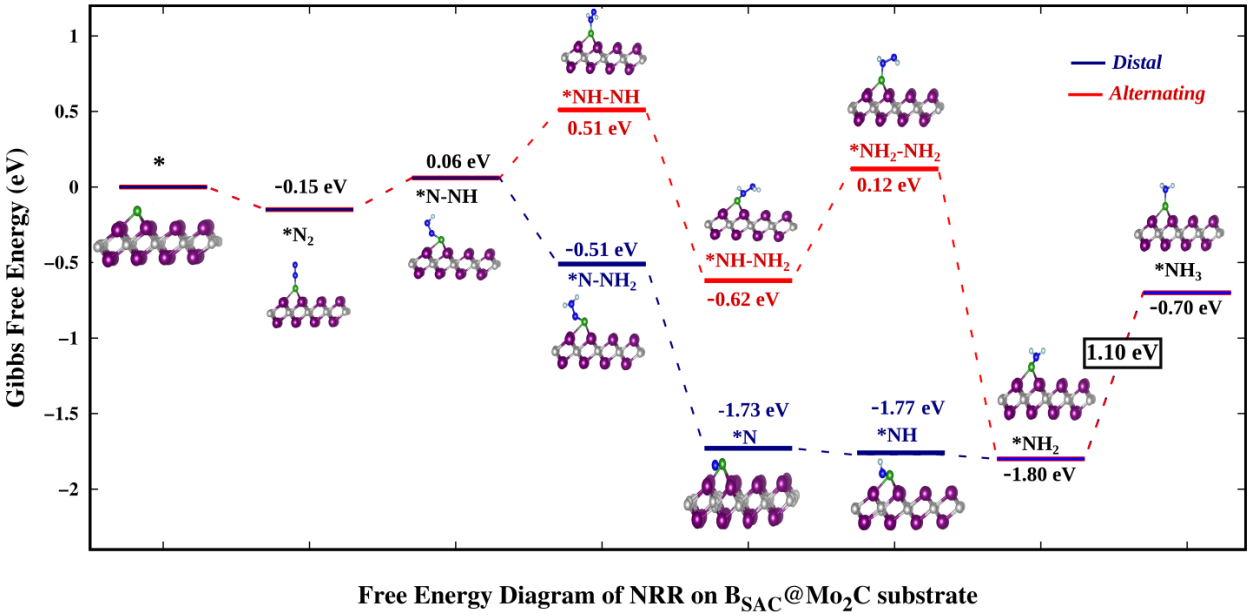


Figure S4: Free energy diagram of distal and alternating routes of Nitrogen Reduction Reaction (NRR) on B_{SAC}@Mo_2C

Table S4. Details of Gibbs free energies of N_xH_y intermediates, Bader charges and N-N bond length for NRR on $B_{SAC}@Mo_2C$

		ZPE (eV)	TS (eV)	G (eV)	Q-B	Q-N_{avg}	N-N bond (Å)
	*	0	0	-470.10	-0.58	_	
Distal	*N_2	0.22	0.17	-487.32	0.05	-0.28	1.1424
	*N-NH	0.52	0.13	-490.53	0.26	-0.67	1.2627
	*N-NH_2	0.84	0.16	-494.52	0.36	-0.91	1.3383
	*N	0.10	0.03	-480.36	0.47	-1.62	
	*NH	0.39	0.04	-483.83	0.31	-1.66	
	*NH_2	0.74	0.07	-487.28	0.23	-1.57	
	*NH_3	1.04	0.14	-490.00	-0.10	-1.32	
Alternating	*N_2	0.22	0.17	-487.32	0.05	-0.28	1.1424
	*N-NH	0.52	0.13	-490.53	0.26	-0.67	1.2627
	*NH-NH	0.84	0.21	-493.49	0.11	-0.65	1.2894
	*NH-NH_2	1.17	0.16	-498.04	0.21	-0.96	1.4492
	*NH_2-NH_2	1.50	0.23	-500.73	-0.07	-0.89	1.479
	*NH_2	0.74	0.07	-487.28	0.22	-1.57	
	*NH_3	1.04	0.14	-490.00	-0.10	-1.32	

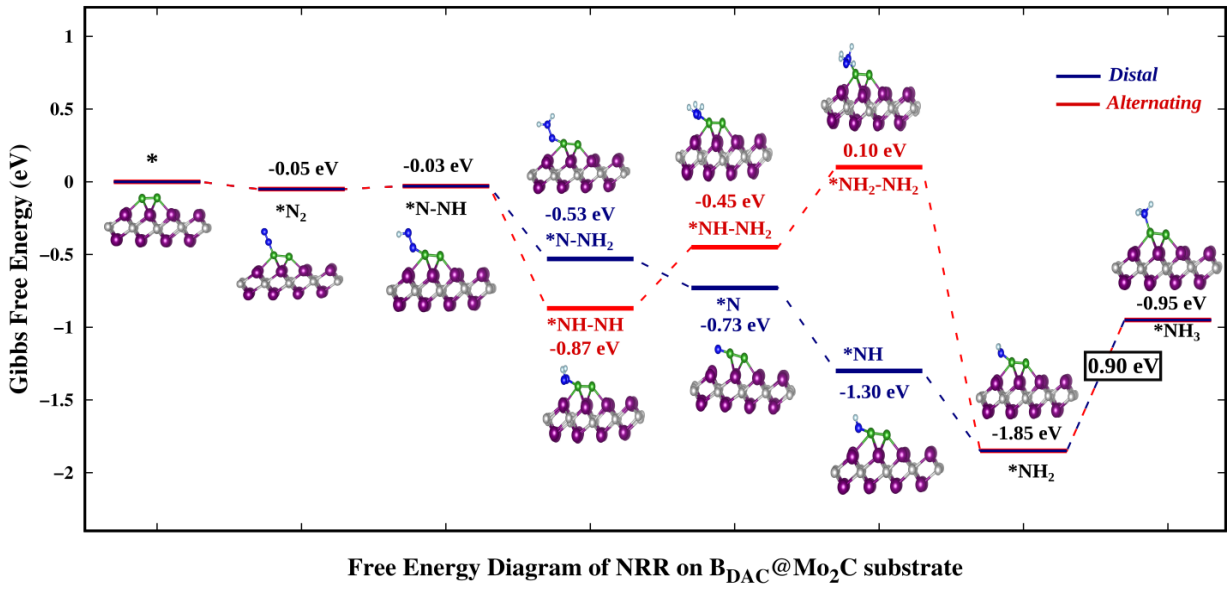


Figure S5: Free energy diagram of distal and alternating routes of Nitrogen Reduction Reaction (NRR) on $B_{DAC}@Mo_2C$

Table S5. Details of Gibbs free energies of N_xH_y intermediates, Bader charges and N-N bond length for NRR on $B_{DAC}@Mo_2C$

		ZPE (eV)	TS (eV)	G (eV)	Q-B	Q-N_{avg}	N-N bond (Å)
	*	0	0	-477.34	-0.46	_	
Distal	*N_2	0.22	0.16	-494.46	-0.16	-0.25	1.137
	*N-NH	0.53	0.12	-497.86	-0.01	-0.66	1.2623
	*N-NH_2	0.84	0.16	-501.78	-0.02	-0.86	1.3236
	*N	0.10	0.04	-486.61	0.10	-1.43	
	*NH	0.39	0.06	-490.60	0.06	-1.57	
	*NH_2	0.74	0.06	-494.57	-0.06	-1.53	
	*NH_3	1.05	0.13	-497.50	-0.26	-1.36	
Alternating	*N_2	0.22	0.16	-494.46	-0.16	-0.25	1.137
	*N-NH	0.53	0.12	-497.86	-0.01	-0.66	1.2623
	*NH-NH	0.83	0.10	-502.12	0.11	-0.65	1.4366
	*NH-NH_2	1.20	0.10	-505.82	0.21	-0.96	1.4749
	*NH_2-NH_2	1.50	0.14	-507.99	-0.07	-0.89	1.4894
	*NH_2	0.74	0.06	-494.57	0.22	-1.57	
	*NH_3	1.05	0.13	-497.50	-0.10	-1.32	

Table S6. Details of Gibbs free energies of N_xH_y intermediates, Bader charges and N-N bond length for NRR on $B_{SAC}@Mo_2C$-Mo_{vac}

		ZPE (eV)	TS (eV)	G (eV)	Q-B	Q-N_{avg}	N-N bond (Å)
	*	0	0	-456.96	-0.41	_	
Distal	*N_2	0.22	0.16	-474.74	0.08	-0.31	1.1457
	*N-NH	0.52	0.13	-478.51	0.25	-0.69	1.2634
	*N-NH_2	0.83	0.18	-482.50	0.32	-0.86	1.3225
	*N	0.09	0.03	-467.89	0.42	-1.59	
	*NH	0.39	0.05	-471.73	0.41	-1.71	
	*NH_2	0.73	0.08	-474.69	0.26	-1.56	
	*NH_3	1.04	0.14	-477.94	-0.11	-1.36	

Alternating	*N_2	0.22	0.16	-456.96	0.08	-0.31	1.1457
	*N-NH	0.52	0.13	-474.74	0.25	-0.69	1.2634
	*NH-NH	0.83	0.23	-478.51	0.27	-0.69	1.297
	*NH-NH_2	1.16	0.16	-480.88	0.32	-0.97	1.4556
	*NH_2-NH_2	1.45	0.22	-485.39	0.16	-0.92	1.4743
	*NH_2	0.73	0.08	-474.69	0.26	-1.56	
	*NH_3	1.04	0.14	-477.94	-0.11	-1.36	
Enzymatic	*N_2	0.20	0.09	-475.42	0.55	-0.77	1.2714
	*N-NH	0.52	0.08	-479.25	0.56	-0.91	1.3463
	*NH-NH	0.83	0.10	-482.53	0.36	-0.99	1.455
	*NH-NH_2	1.16	0.12	-485.99	0.30	-1.02	1.5148
	*NH_2-NH_2	1.42	0.15	-491.89	0.32	-1.46	3.6384
	*NH_2	0.73	0.08	-474.69	0.26	-1.56	
	*NH_3	1.04	0.14	-477.94	-0.11	-1.36	

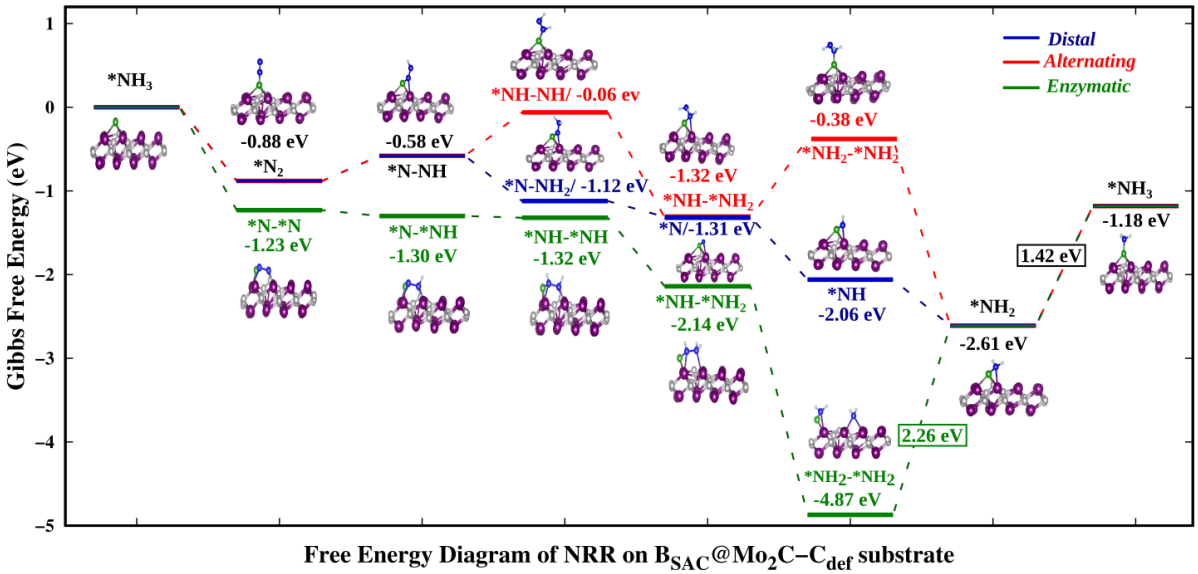


Figure S6: Free energy diagram of distal, alternating and enzymatic routes of Nitrogen Reduction Reaction (NRR) on $B_{SAC}@Mo_2C$-C_{def}

Table S7. Details of Gibbs free energies of N_xH_y intermediates, Bader charges and N-N bond length for NRR on $B_{SAC}@Mo_2C$-C_{def}

		ZPE (eV)	TS (eV)	G (eV)	Q-B	Q-N_{avg}	N-N bond (Å)
	*	0	0	-465.12	-0.37	_	
Distal	*N_2	0.23	0.16	-483.07	0.82	-0.30	1.1444
	*N-NH	0.52	0.12	-486.18	1.04	-0.64	1.2615
	*N-NH_2	0.85	0.14	-490.14	1.08	-0.87	1.3396
	*N	0.10	0.03	-474.96	1.36	-1.46	
	*NH	0.39	0.06	-479.13	1.22	-1.56	
	*NH_2	0.74	0.06	-483.10	1.02	-1.52	
	*NH_3	1.05	0.15	-485.50	0.69	-1.35	
Alternating	*N_2	0.23	0.16	-483.07	0.82	-0.30	1.1444
	*N-NH	0.52	0.12	-486.18	1.04	-0.64	1.2615
	*NH-NH	0.84	0.18	-489.09	0.96	-0.69	1.3045
	*NH-NH_2	1.18	0.17	-493.77	1.00	-0.94	1.4481
	*NH_2-NH_2	1.51	0.26	-496.25	0.71	-0.88	1.4759
	*NH_2	0.74	0.06	-483.10	1.02	-1.52	
	*NH_3	1.05	0.15	-485.50	0.69	-1.35	
Enzymatic	*N_2	0.24	0.04	-483.41	0.64	-0.96	1.4242
	*N-NH	0.57	0.05	-486.90	0.62	-1.01	1.4606
	*NH-NH	0.88	0.06	-490.34	0.26	-0.96	1.4892
	*NH-NH_2	1.19	0.11	-494.58	0.148	-0.98	1.4762
	*NH_2-NH_2	1.44	0.14	-500.73	0.218	-1.40	4.6108
	*NH_2	0.74	0.06	-483.10	1.02	-1.52	
	*NH_3	1.05	0.15	-485.50	0.69	-1.35	