Electronic Supplementary Material (ESI) for RSC Advances.

Supplementary Information

Influence of enolate/epoxy configuration, doping and vacancy on the catalyticactivity of graphene

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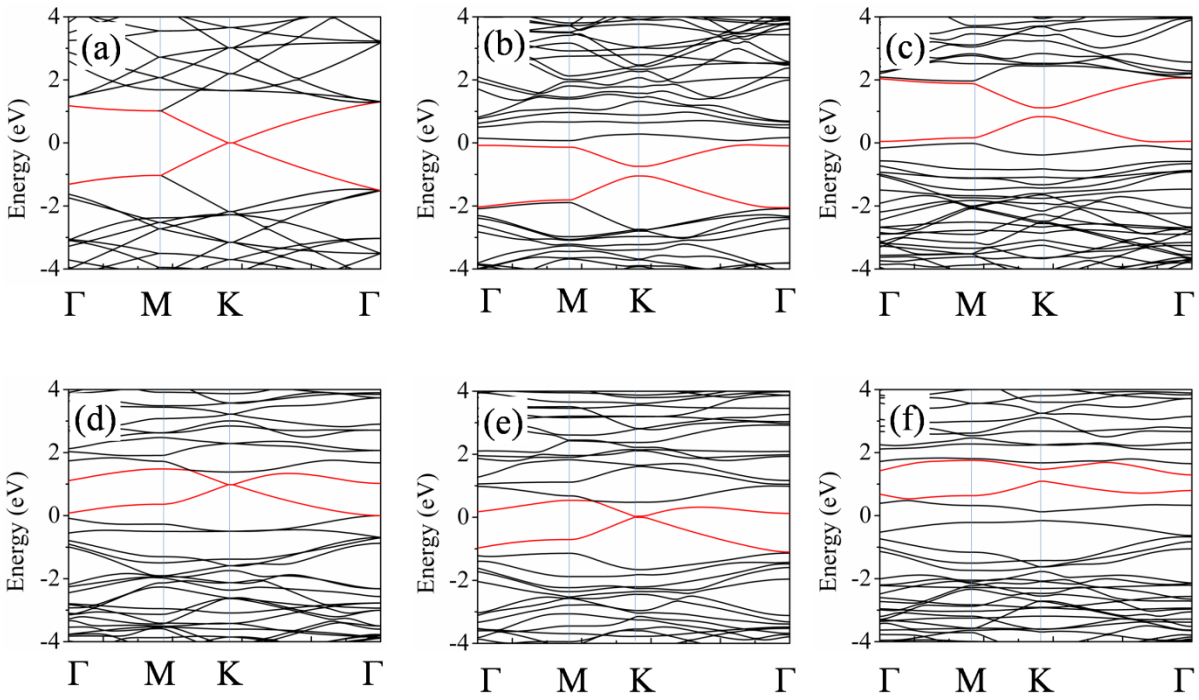

Fig. S1: Band structures of some graphitic systems chosen in this study (a) pristine graphene (b) 2N-P (c) 2B-P (d) undoped DV (e) 2N-DV (f) 2B-DV. The Fermi level is set at zero. Red band with lower and higher energy indicates the π and π^* band respectively.

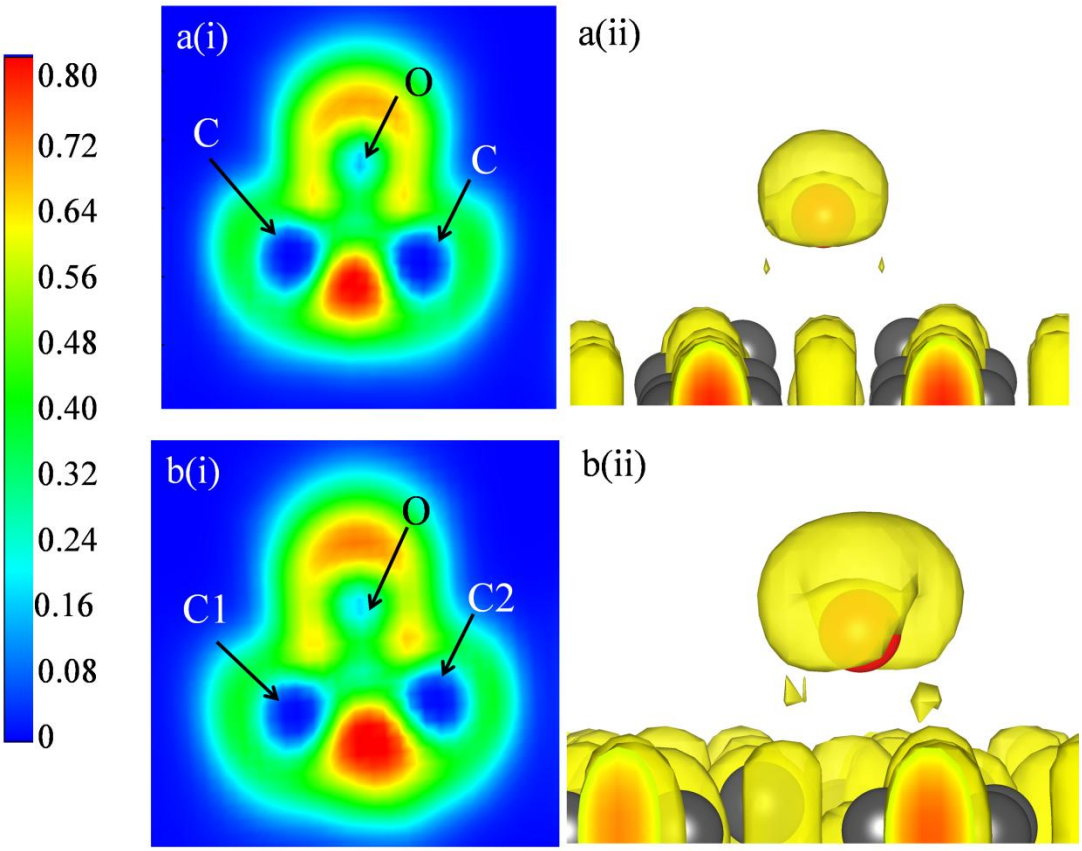

Fig. S2: Electron Localization Function (ELF) contours and isosurface (isovalue = 0.62) of epoxide configured O atom adsorbed on (a) pristine graphene (b) undoped-DV surfaces.

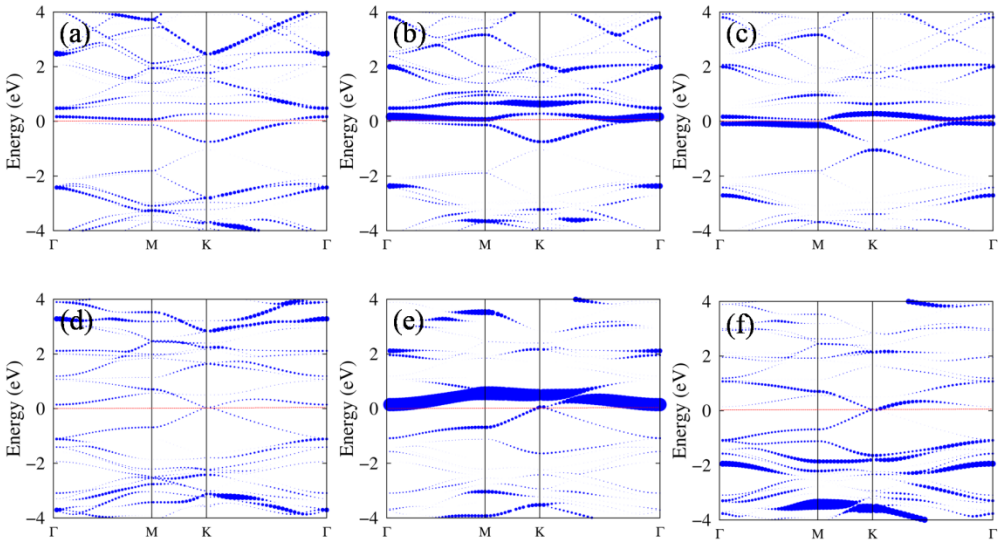

Fig. S3: p_z projected band structures of: (a) & (d) a carbon atom far from the dopant of 2N-P and 2N-DV respectively, (b) & (e) the carbon atom adjacent to the dopant of 2N-P and C1 atom of 2N-DV surface respectively, (c) & (f) one nitrogen dopant of 2N-P and 2N-DV respectively. The Fermi level is at zero.

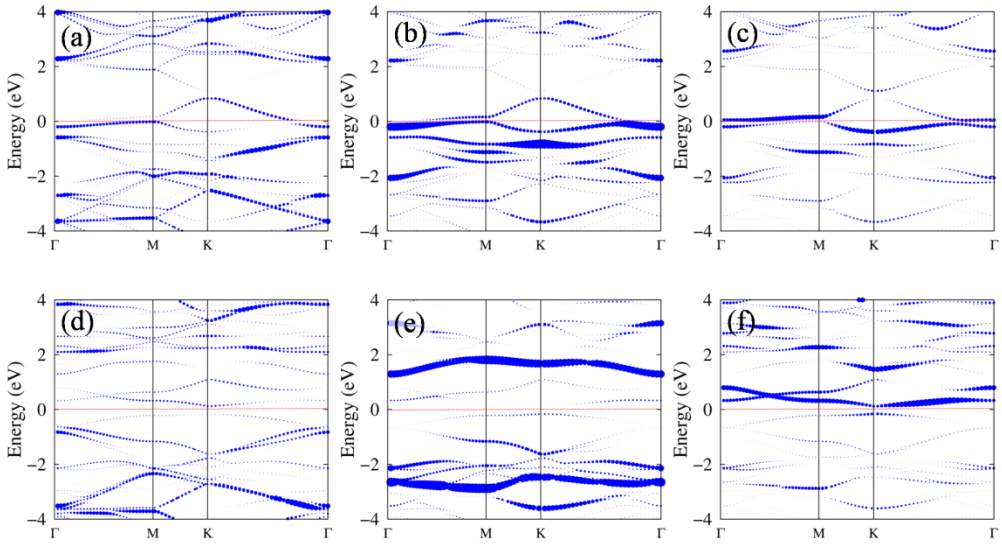

Fig. S4: p_z projected band structures of : (a) & (d) a carbon atom far from the dopant of 2B-P and 2B-DV respectively, (b) & (e) the carbon atom adjacent to the dopant of 2B-P and C1 atom of 2B-DV surface respectively, (c) & (f) one boron dopant of 2B-P and 2B-DV respectively. The Fermi level is at zero.

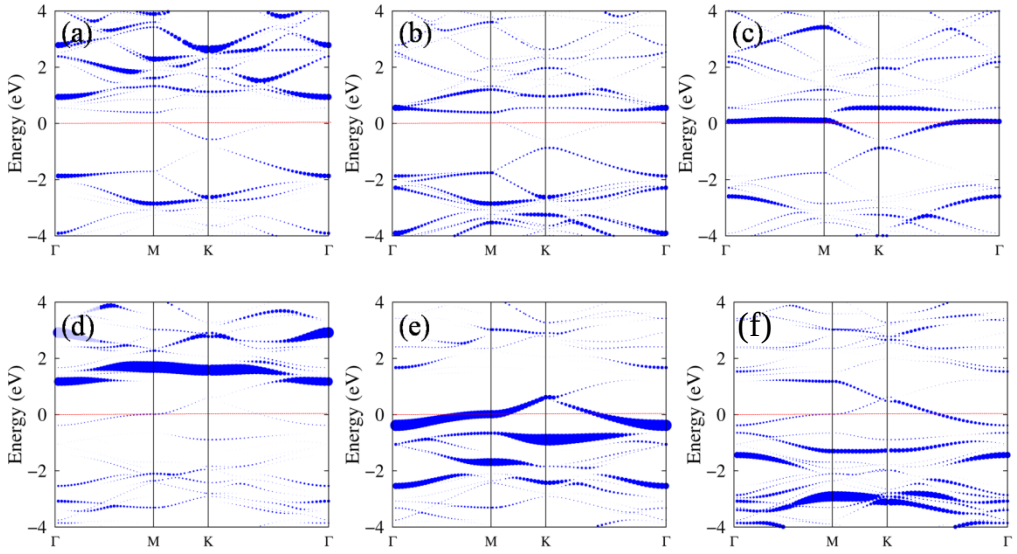

Fig. S5: p_z projected band structures of: (a) & (d) the borondopant of B2N-P and B2N-DV respectively, (b) & (e) the carbon atom adjacent to boron of B2N-P and C2 atom of B2N-DV surface respectively, (c) & (f) one nitrogen dopant of B2N-P and B2N-DV respectively. The Fermi level is at zero.

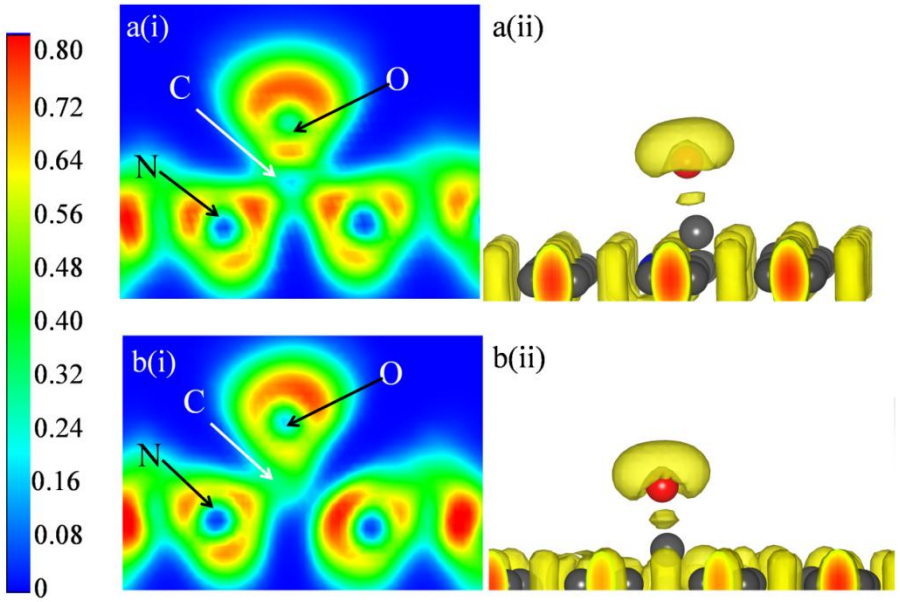

Fig.S6: Electron Localization Function (ELF) contours and isosurface (isovalue = 0.62) of enolate configured O atom adsorbed on (a) 2N-P (b) 2N-DV surfaces.

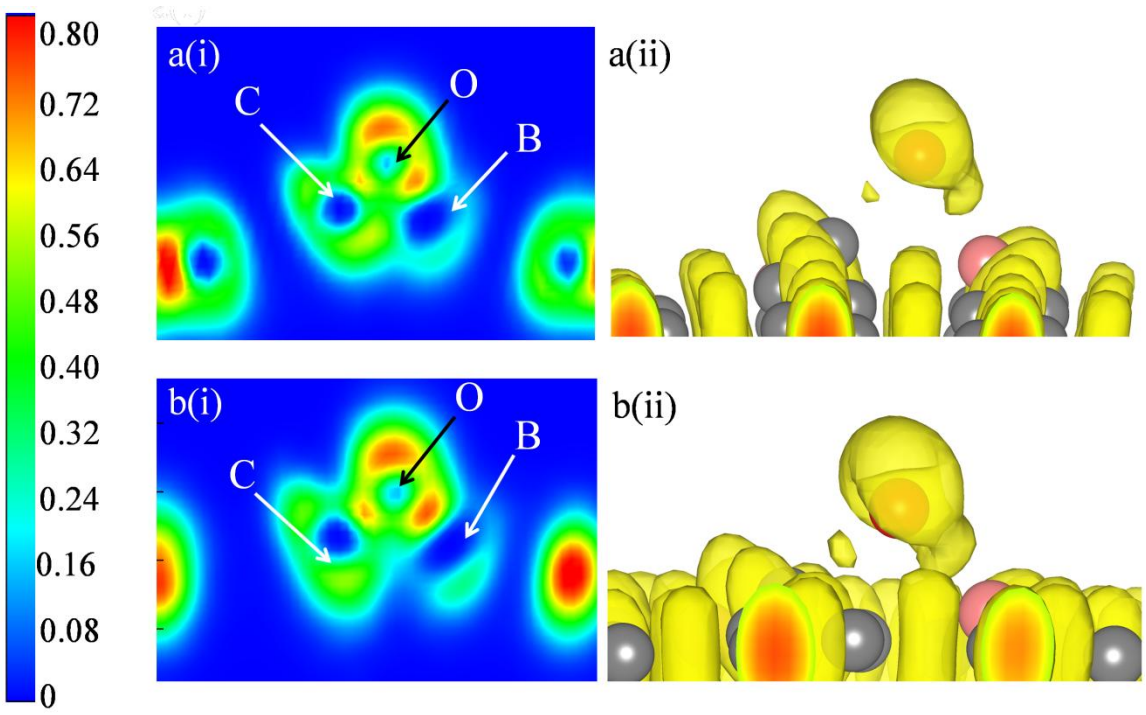

Fig. S7: Electron Localization Function (ELF) contours and isosurface (isovalue = 0.62) of epoxide configured O atom adsorbed on (a) 2B-P (b) 2B-DV surfaces.

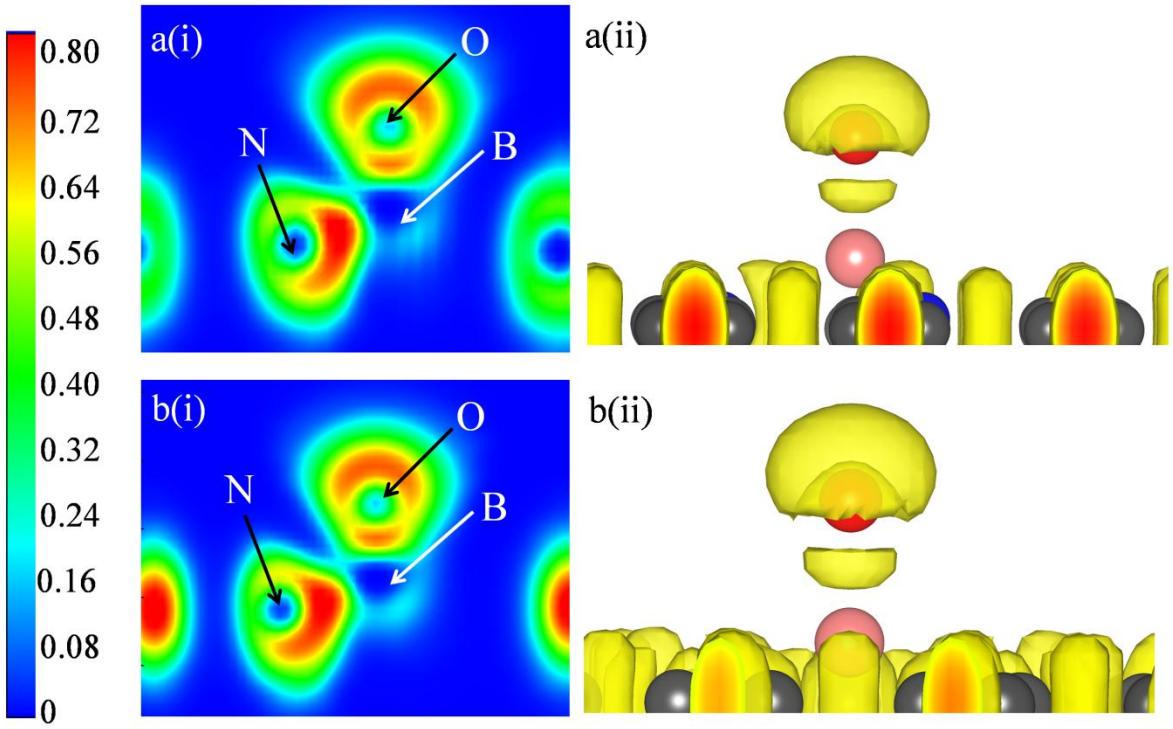

Fig. S8: Electron Localization Function (ELF) contours and isosurface (isovalue = 0.62) of epoxide configured O atom adsorbed on (a) B3N-P (b) B3N-DV surfaces

Table S1: Bader charges on the active sites before and after O adsorption and on the adsorbed O atom. @ indicate replaced C atom site. Bader charge unit is |e|

System	Site	Bader charge before O adsorption	Bader charge after O adsorption	Bader charge on O
Pristine graphene	C	-0.09, +0.1	+0.27, +0.38	-0.79
Undoped- DV	C1	+0.03	+0.38	-0.82
	C2	-0.01	+0.42	
2N-P	N	-1.22	-1.12	-1.09
	C	+0.73	+1.2	
2N-DV	C1	+0.59	+1.17	-1.02
2B-P	B	+1.84	+1.97	-1.28
	C	-1.183	-0.22	
2B-DV	B (@C2)	+1.83	+1.96	-1.24
	C1	-1.28	-0.22	
B2N-P	B	+1.98	+2.07	-1.07
	C	-0.48	-0.05	
	N	-1.46,-1.46	-1.41,-1.41	
B2N-DV	B (@C1)	+1.96	+2.025	-1.12
	C (@C2)	-0.68	+0.015	
	N (@C2)	-1.2,-1.2	-1.2,-1.2	
B3N-P	B	+2.11	+2.19	-1.31
	N	-1.5	-1.36	
B3N-DV	B (@C1)	+2.07	+2.11	-1.24
	N (@C2)	-1.26,-1.23,-1.24	-1.08, -1.08	

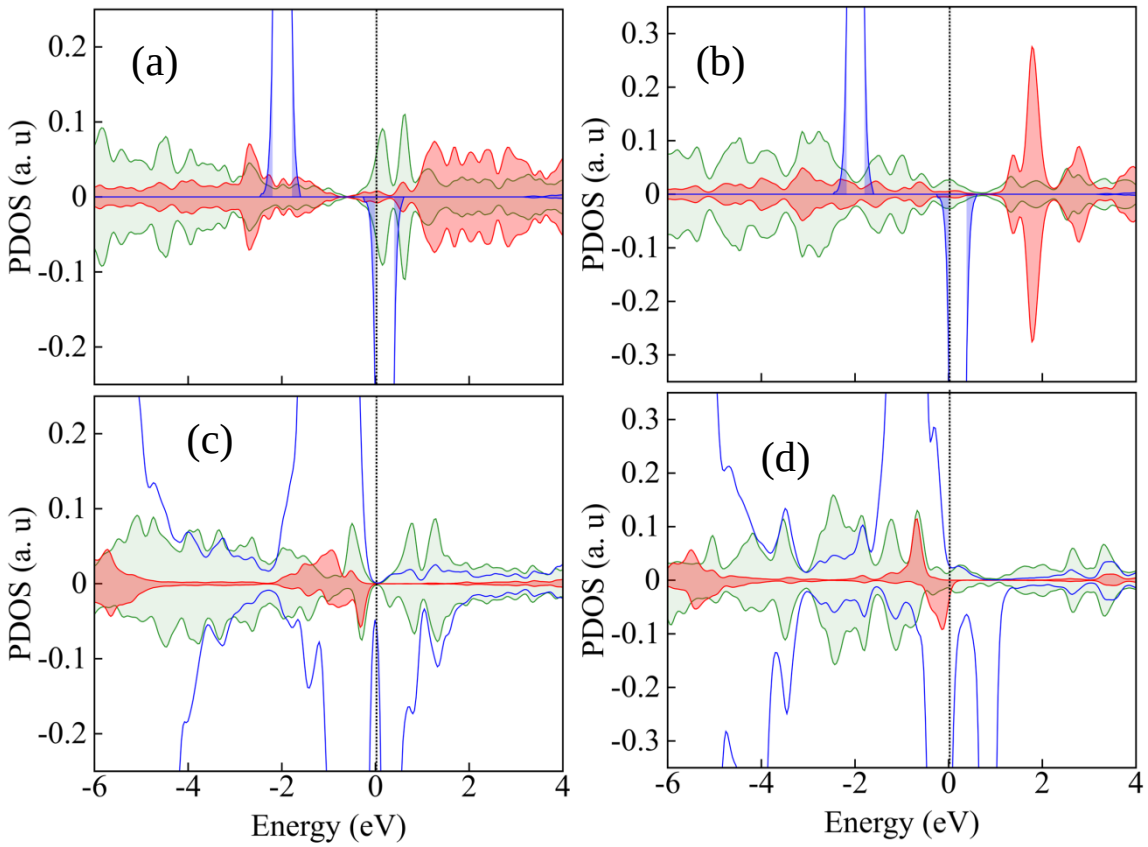

Fig. S9: Partial density of states of surface atoms and O_2 molecule, (a),(c) before and after O_2 adsorption on B2N -P, (b),(d) before and after O_2 adsorption on B2N-DV. The red and green shaded plots represent the p_z orbital projected density of states of the central boron atom and a neighboring nitrogen dopant respectively. The blue plot indicates the p states of the oxygen molecule.

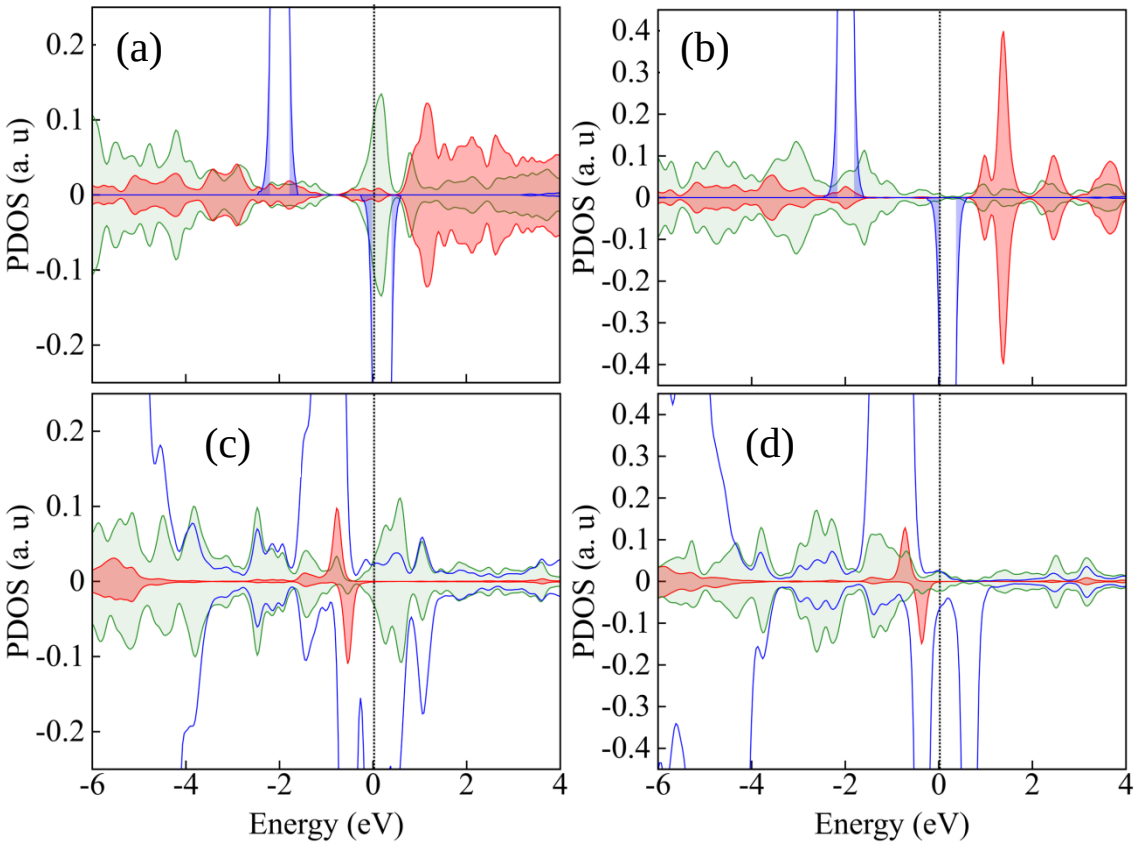

Fig. S10: Partial density of states of surface atoms and O_2 molecule, (a),(c) before and after O_2 adsorption on B3N -P, (b), (d) before and after O_2 adsorption on B3N-DV. The red and green shaded plots represent the p_z orbital projected density of states of the central boron atom and a neighboring nitrogen dopant respectively. The blue plot indicates the p states of the oxygen molecule.

System	CO Adsorption Energy (eV)	
	PBE	PBE+D
2N-P	0.099	-0.060
2N-DV	0.056	-0.067
2B-P	0.042	-0.153
2B-DV	0.065	-0.068
B2N-P	0.035	-0.102
B2N-DV	0.058	-0.067
B3N-P	0.044	-0.102
B3N-DV	0.029	-0.088

Table S2: CO molecule adsorption energies on the studied graphitic systems.

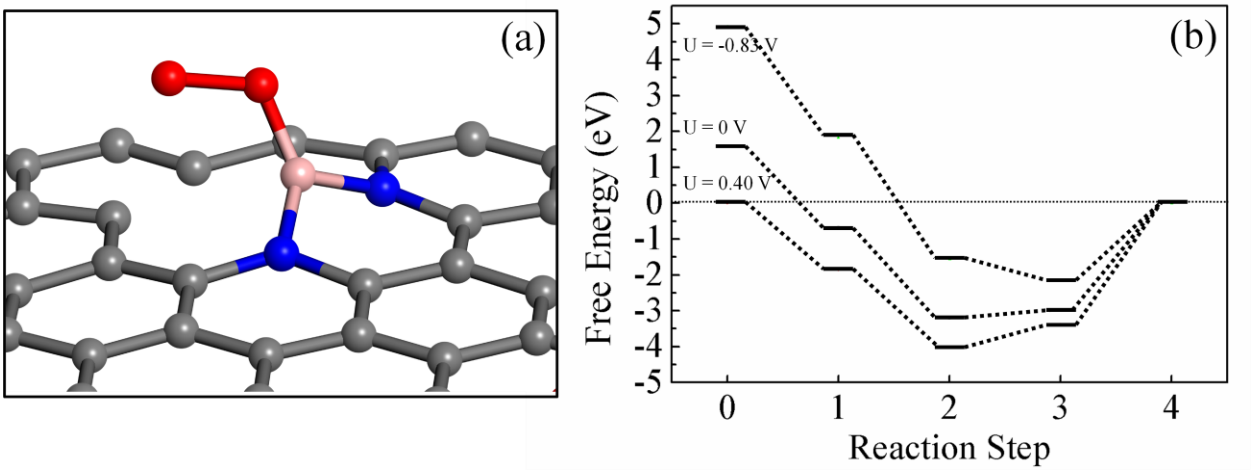

Fig. S11: (a)Optimized geometry of oxygen molecule adsorbed on a B2N-SV defect. (b) ORR free energy profile on B2N-SV.

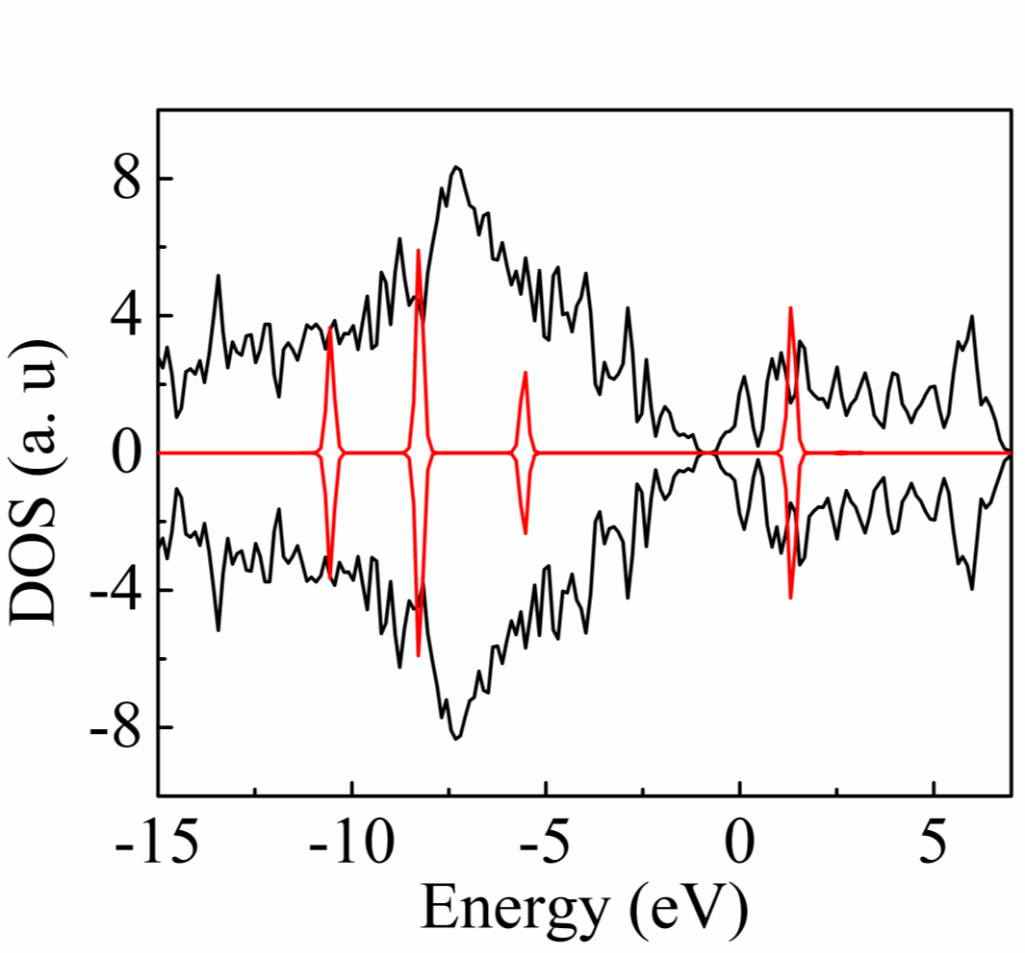

Fig. S12: Interaction of CO with a graphitic surface. The B3N-P surface is shown here as an example. The black line represents the PDOS of the surface only and the red plot represents the PDOS of CO molecule when they do not interact with each other.