A DFT study of B-doped graphene as a metal-anchor: effects of oxidation and strain

SUPPLEMENTARY INFORMATION

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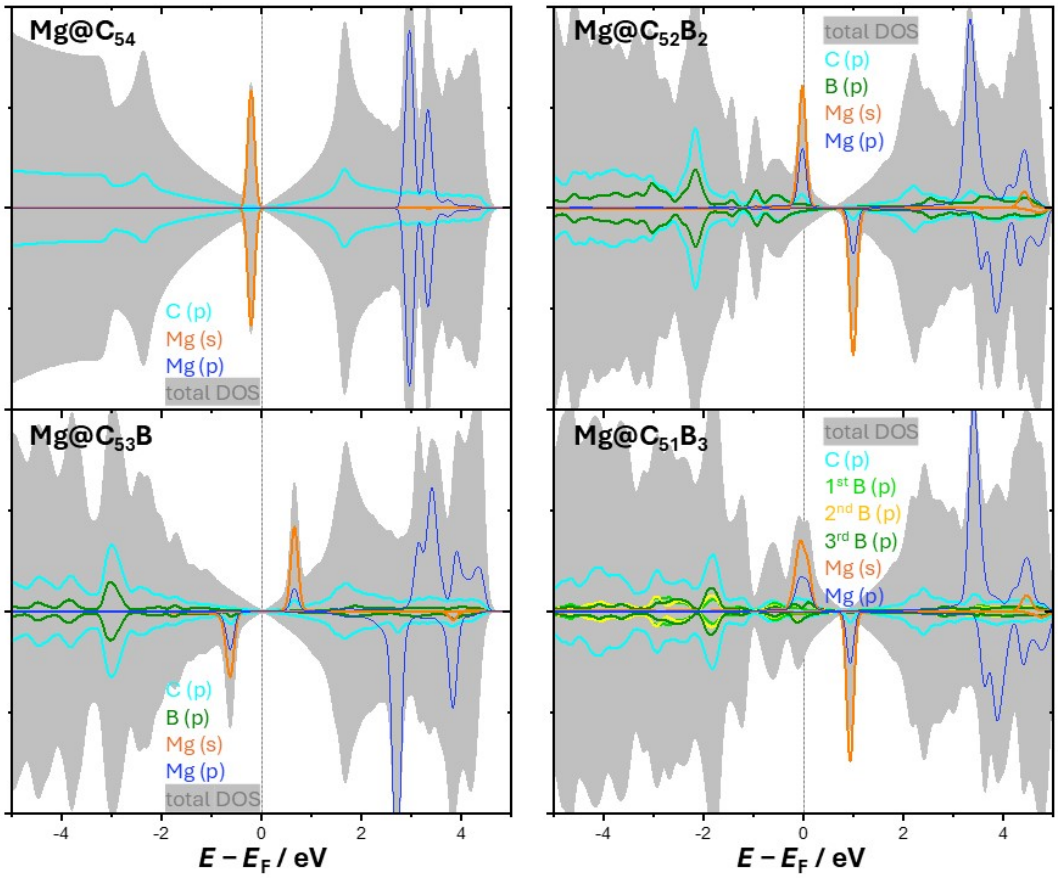

Figure SI1. Density of states (DOS) for Mg adsorbed on pristine graphene (C_{54}) and B-doped graphene ($C_{54-n}B_n$, $n \in \{0, 1, 2, 3\}$) at their preferred adsorption sites.

Table SI1. Metal adsorption energies onto $C_{54-n}B_n$, referred to isolated metal atoms (E_{ads}) and to metal atoms in pure metallic phase (ΔE, calculated using metal cohesive energy). Metal aggregation is favored over metal-substrate interaction for $\Delta E > 0$ (numbers given in red).

n	Mg@$C_{54-n}B_n$		Zn@$C_{54-n}B_n$		Cu@$C_{54-n}B_n$		Pt@$C_{54-n}B_n$	
	E_{ads} / eV	ΔE / eV	E_{ads} / eV	ΔE / eV	E_{ads} / eV	ΔE / eV	E_{ads} / eV	ΔE / eV
0	−0.11	1.40	−0.18	1.17	−0.59	2.90	−2.05	3.79
1	−0.98	0.53	−0.24	1.11	−1.69	1.80	−2.71	3.13
2	−1.45	0.06	−0.35	1.00	−2.17	1.32	−3.26	2.59
3	−1.30	0.21	−0.43	0.92	−2.04	1.45	−3.40	2.44

Table SI2. Metal adsorption energies onto epoxy-group containing boron-doped graphene, $C_{54-n}B_nO$, referred to isolated metal atoms (E_{ads}) and to metal atoms in pure metallic phase (ΔE, calculated using metal cohesive energy). Metal aggregation is favored over metal-substrate interaction for $\Delta E > 0$ (numbers given in red).

n	Mg@$C_{54-n}B_nO$		Zn@$C_{54-n}B_nO$		Cu@$C_{54-n}B_nO$		Pt@$C_{54-n}B_nO$	
	E_{ads} / eV	ΔE / eV	E_{ads} / eV	ΔE / eV	E_{ads} / eV	ΔE / eV	E_{ads} / eV	ΔE / eV
0	−1.75	−0.24	−0.17	1.18	−2.61	0.88	−2.26	3.58
1	−1.49	0.02	−0.19	1.16	−1.71	1.78	−2.83	3.01
2	−1.87	−0.36	−0.50	0.85	−2.06	1.43	−3.44	2.40
3	−1.49	0.02	−0.42	0.93	−1.90	1.59	−3.53	2.31

Table SI3. Metal adsorption energies onto hydroxyl-functionalized boron-doped graphene, $C_{54-n}B_nOH$, referred to isolated metal atoms (E_{ads}) and to metal atoms in pure metallic phase (ΔE, calculated using metal cohesive energy). Metal aggregation is favored over metal-substrate interaction for $\Delta E > 0$ (numbers given in red).

n	Mg@$C_{54-n}B_nOH$		Zn@$C_{54-n}B_nOH$		Cu@$C_{54-n}B_nOH$		Pt@$C_{54-n}B_nOH$	
	E_{ads} / eV	ΔE / eV	E_{ads} / eV	ΔE / eV	E_{ads} / eV	ΔE / eV	E_{ads} / eV	ΔE / eV
0	−2.82*	−1.31*	−1.42*	−0.07*	−4.02*	−0.53*	−4.61*	1.23*
1	−3.55	−2.04	−0.43	0.92	−2.08	1.42	−2.77	3.07
2	−3.69	−2.18	−0.72	0.63	−2.73	0.76	−3.21	2.64
3	−3.56	−2.05	−1.11	0.24	−3.06	0.43	−3.42	2.42

*MOH phase separation

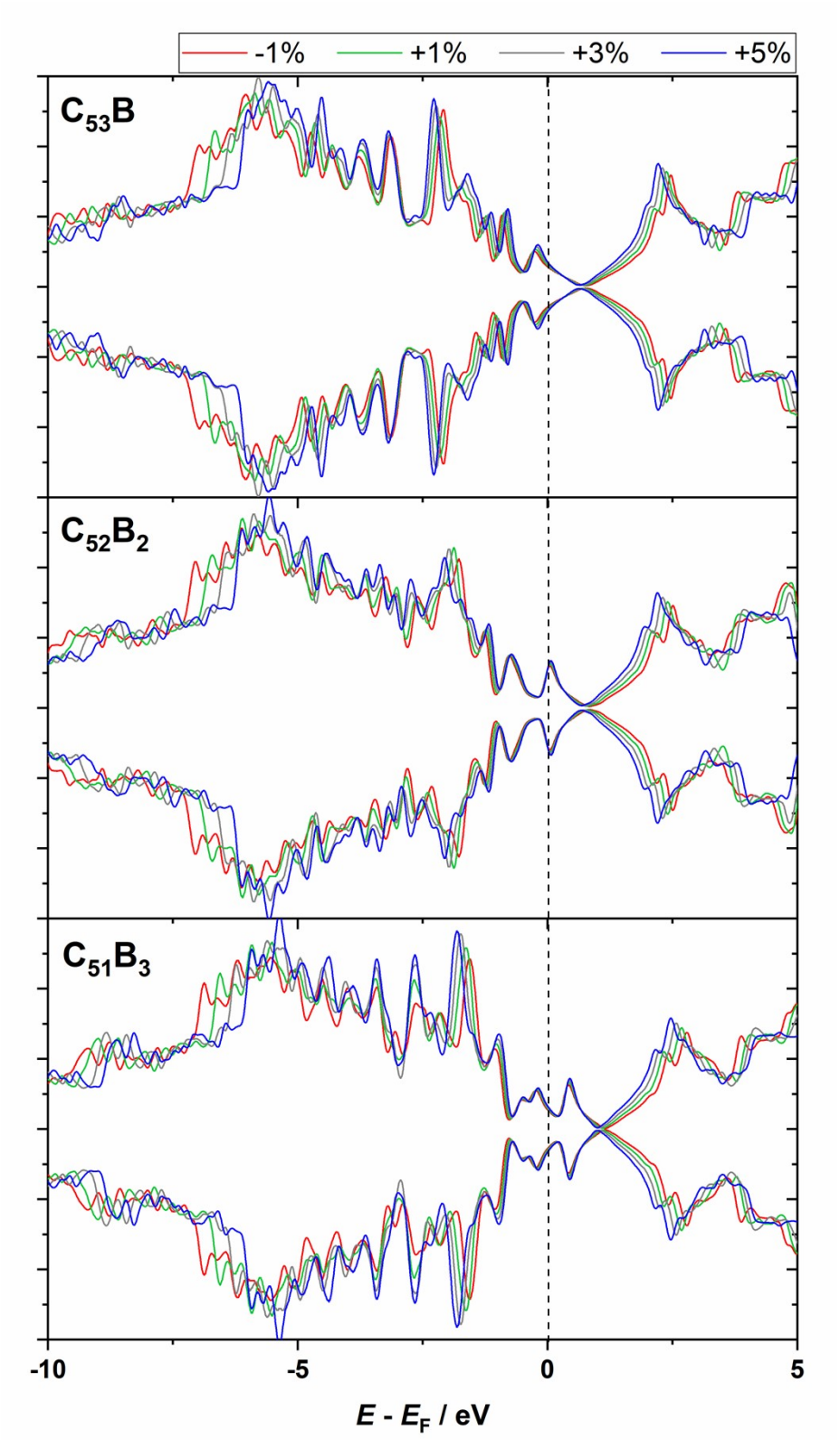

Figure SI2. Total densities of states of strained $C_{53}B$, $C_{52}B_2$ and $C_{51}B_3$ systems, with strain levels of −1%, +1%, +3% and +5%.

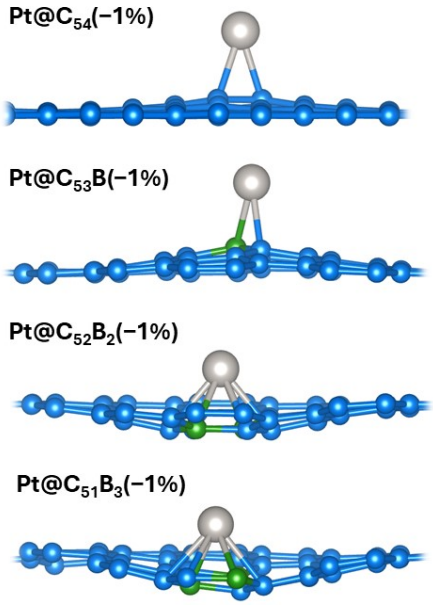

Figure SI3. Optimized structures of Pt interacting with $C_{54-n}B_n$ models compressed by 1% ($n \in \{0, 1, 2, 3\}$).

Table SI4. Adsorption of H onto Pt on $C_{54-n}B_n$ and their oxidized forms. Adsorption energies are calculated with respect to isolated H atom (E_{ads}(H)) and ½ of H_2 molecule (E_{ads}(1/2H_2)). The last column shows Gibbs free energy of H adsorption ($\Delta G(H_{ads})$).

System (H@Pt@subs)	E_{ads}(H) / eV	E_{ads}(1/2H_2) / eV	$\Delta G(H_{ads})$ / eV
H@Pt@C_{54}	−2.82	−0.57	−0.33
H@Pt@$C_{53}B$	−3.07	−0.82	−0.58
H@Pt@$C_{52}B_2$	−3.01	−0.76	−0.52
H@Pt@$C_{51}B_3$	−3.03	−0.79	−0.55
H@Pt@$C_{54}O$	−2.71	−0.47	−0.23
H@Pt@$C_{53}BO$	−2.92	−0.67	−0.43
H@Pt@$C_{52}B_2O$	−2.89	−0.65	−0.41
H@Pt@$C_{51}B_3O$	−2.80	−0.55	−0.31
H@Pt@$C_{53}BOH$	−2.75	−0.51	−0.27
H@Pt@$C_{52}B_2OH$	−2.83	−0.58	−0.34
H@Pt@$C_{51}B_3OH$	−2.75	−0.51	−0.27

Table SI5. Adsorption energies of CO onto Cu on $C_{54-n}B_n$ and their oxidized forms, with corresponding bond lengths (d) between Cu and C from CO, and C and O in adsorbed CO.

System (CO@Cu@subs)	E_{ads}(CO) / eV	d(Cu−C) / Å	d(C−O) / Å

CO@Cu@C_{54}	−1.60	1.78	1.16
CO@Cu@$C_{53}B$	−1.99	1.78	1.15
CO@Cu@$C_{52}B_2$	−2.09	1.78	1.15
CO@Cu@$C_{51}B_3$	−2.04	1.78	1.15
CO@Cu@$C_{53}BO$	−2.08	1.77	1.15
CO@Cu@$C_{52}B_2O$	−1.90	1.78	1.15
CO@Cu@$C_{51}B_3O$	−1.94	1.78	1.15
CO@Cu@$C_{53}BOH$	−1.97	1.77	1.15
CO@Cu@$C_{52}B_2OH$	−1.79	1.78	1.15
CO@Cu@$C_{51}B_3OH$	−1.74	1.78	1.15

Table SI6. Adsorption energies of CO_2 onto Cu on $C_{54-n}B_n$ and their oxidized forms, with corresponding bond lengths (*d*) between Cu and C and/or O from CO_2, and C and O in adsorbed CO_2.

System (CO_2@Cu@subs)	E_{ads}**(CO) / eV**	***d*(Cu-C/O) / Å**	d_1**(C−O) / Å**	d_2**(C−O) / Å**	∠**(O−C−O) / ⁰**
CO_2@Cu@C_{54}	−0.37	C 1.99 O 2.00	1.27	1.20	146.3
CO_2@Cu@$C_{53}B$	−0.49	C 2.14 O 1.96	1.23	1.18	161.1
CO_2@Cu@$C_{52}B_2$	−0.50	C 2.05 O 2.00	1.23	1.19	156.4
CO_2@Cu@$C_{51}B_3$	−0.49	C 2.09 O 2.00	1.23	1.19	157.4
CO_2@Cu@$C_{53}BO$	−0.62	C 2.00 O 1.97	1.24	1.19	154.3
CO_2@Cu@$C_{52}B_2O$	−0.55	O 1.99	1.19	1.17	178.1
CO_2@Cu@$C_{51}B_3O$	−0.53	O 1.99	1.19	1.17	179.0
CO_2@Cu@$C_{53}BOH$	−0.45	O 2.01	1.18	1.17	179.4
CO_2@Cu@$C_{52}B_2OH$	−0.30	O 2.12	1.19	1.17	179.6
CO_2@Cu@$C_{51}B_3OH$	−0.31	O 2.08	1.18	1.17	179.6