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Supporting Information for

Thermodynamic Mechanism of Controllable Growth of Two-Dimensional Uniformly Ordered Boron Doped Graphene

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I. Derivation of Eqs. (5) and (6) in Main Text:

The chemical potential $\mu_{C(CH_4)}$, $\mu_{B(B_2H_6)}$ under different temperatures and pressures can be defined as follows:

$$\mu_{C(CH_4)}(T,P) \equiv G_{CH_4}(T,P) - 2G_{H_2}(T,P) = G_{CH_4}(T,P) - 4\mu_{H(H_2)}(T,P)$$
$$\mu_{B(B_2H_6)}(T,P) \equiv G_{B_2H_6}(T,P) - 3G_{H_2}(T,P) = G_{B_2H_6}(T,P) - 6\mu_{H(H_2)}(T,P) \#(S1)$$

Under any temperature and pressure, the difference of chemical potential between carbon (boron) feedstocks and graphene (B_{12}) can be defined as follows:

$$\triangle \mu_{C(CH_4)}(T,P) \equiv \mu_{C(CH_4)}(T,P) - \mu_{C(Gr)}(0)$$
$$\triangle \mu_{B(B_2H_6)}(T,P) \equiv \mu_{B(B_2H_6)}(T,P) - \mu_{B(B_{12})}(0) \#^{\#(S2)}$$

Defining the free energy of the carbon (boron) feedstocks from the ground state to compounds state under temperature T and pressure P:

$$\triangle {}_f G_{CH_4}(T,P) = G_{CH_4}(T,P) - \mu_{C(Gr)}(T,P) - 4\mu_{H(H_2)}(T,P)$$
$$\triangle {}_f G_{B_2H_6}(T,P) = G_{B_2H_6}(T,P) - \mu_{B(B_{12})}(T,P) - 6\mu_{H(H_2)}(T,P)^{\#(S3)}$$

Assuming that $\mu_{C(Gr)}(T,P) \approx \mu_{C(Graphite)}$, using formula (S1)(S2)(S3), it can be derived:

$$\triangle \mu_{C(CH_4)}(T,P) = \triangle {}_f G_{CH_4}(T,P) + \triangle {}_T G_{Gr}(T)$$
$$\triangle \mu_{B(B_2H_6)}(T,P) = \triangle {}_f G_{B_2H_6}(T,P) + \triangle {}_T G_{B_{12}}(T) \#(S4)$$

$$\mu_{C(Gr)}(T) = \mu_{C(Gr)}(0) + \triangle {}_T G_{Gr}(T)$$
In particular, $$\mu_{B(B_2H_6)}(T) = \mu_{B(B_{12})}(0) + \triangle {}_T G_{B_{12}}(T) \#(S5)$$

Derived from formula (S2), (S4) and (S5), we have:

$$\mu_{C(CH_4)}(T,P)$$

$$= \mu_{C(Gr)}(T) + \triangle_f G_{CH_4}(T,P) = \mu_{C(Gr)}(T) + \triangle_f G^0_{CH_4}(T) + R$$

$$= \mu_{C(Gr)}(0) + \triangle_T G_{C(Gr)}(T,P^0) + \triangle_f G^0_{CH_4}(T) + RTln\left[\frac{P_{CH_4}}{P^0}\right.$$

$$\mu_{B(B_2H_6)}(T,P)$$

$$= \mu_{B(B_{12})}(T) + \triangle_f G_{B_2H_6}(T,P) = \mu_{B(B_2H_6)}(T) + \triangle_f G^0_{B_2H_6}(T)$$

$$\left[\frac{P_{B_2H_6}}{P^0}\left(\frac{P^0}{P_{H_2}}\right)^2\right]$$

$$= \mu_{B(B_2H_6)}(0) + \triangle_T G_{B(B_2H_6)}(T,P^0) + \triangle_f G^0_{B_2H_6}(T) + RTln$$

$$\left[\frac{P_{B_2H_6}}{P^0}\left(\frac{P^0}{P_{H_2}}\right)^2\right]$$

$$\#(S6)$$

According to the general formula of Gibbs free energy, enthalpy and entropy,

$$G(T,P) = H(T,P) - TS(T) = H^0(T) - TS(T) + RTln\frac{P}{P^0} \#(S7)$$

After transforming (S6), we can get:

$$\triangle \mu_{C\,(CH_4)}(T,P)$$

$$= \mu_{C(CH_4)}(T,P) - \mu_{C(Graphene)}(0) = \left[H^0_{Graphene}(T) - TS\right.$$

$$+ \triangle_f G^0_{CH_4}(T) + RTln\left[\frac{P_{CH_4}}{P^0}\left(\frac{P^0}{P_{H_2}}\right)^2\right]$$

$$\triangle \mu_{B\,(B_2H_6)}(T,P)$$

$$= \mu_{B(B_2H_6)}(T,P) - \mu_{B(B_{12})}(0) = \left[H^0_{B_{12}}(T) - TS^0_{B_{12}}(T) - H^0_{B_{12}}(0)\right]$$

$$+ \triangle_f G^0_{B_2H_6}(T) + RTln\left[\frac{P_{B_2H_6}}{P^0}\left(\frac{P^0}{P_{H_2}}\right)^2\right]$$

Above are the derivations of the difference between chemical potential and carbon (or

boron) in the Feedstocks and Graphene (or B_{12}) under 0 K, among which G represents free energy, T represents temperature, P_X represents the partial pressure of X and P_0 = 0.1MPa represents the standard pressure.

II. The vdW interaction, formation enthalpy (Δ*H*) and lattice mismatch

Table S1. The calculated interfacial vdW interaction of 2D BC_3 and BC_5 on various metal substrates with rotation angles of 0° and 30°. (N/A means the relevant lattice parameters are too large to be calculated)

System	E_{vdW} of 0° (eV per atom)	E_{vdW} of 30° (eV per atom)
BC_3@Cu(111)	-0.256	-0.229
BC_5@Cu(111)	-0.290	-0.272
BC_3@Cu(110)	-0.265	-0.257
BC_5@Cu(110)	-0.268	-0.259
BC_3@Ag(111)	-0.173	-0.159
BC_5@Ag(111)	-0.182	-0.161
BC_3@Ag(110)	-0.154	-0.150
BC_5@Ag(110)	-0.187	-0.185
BC_3@Au(111)	-0.109	-0.106
BC_5@Au(111)	-0.114	-0.108
BC_3@Au(110)	-0.158	-0.154
BC_5@Au(110)	-0.184	-0.155
BC_3@Ir(111)	-0.372	-0.357
BC_5@Ir(111)	-0.325	N/A
BC_3@Ir(110)	-0.425	-0.421
BC_5@Ir(110)	-0.423	-0.411

Table S2. The formation enthalpy (per atom) and lattice mismatch of BC_3 and BC_5 on various metal surfaces, where $B_xC_y@sub$ represent the 2D B-G placed on the corresponding substrates.

System	ΔH (eV/atom)	Lattice mismatch (%)
BC_3@Cu(111)	-0.90	1.45
BC_5@Cu(111)	-0.37	3.11
BC_3@Cu(110)	-0.96	a: 0.12, b:1.90
BC_5@Cu(110)	-1.10	a: 1.88, b: 0.17
BC_3@Ag(111)	-0.23	3.77
BC_5@Ag(111)	-0.44	1.99
BC_3@Ag(110)	-0.45	a: 2.12, b: 2.76
BC_5@Ag(110)	-0.66	a: 3.81, b: 0.60
BC_3@Au(111)	-0.16	2.94
BC_5@Au(111)	-0.13	1.21
BC_3@Au(110)	-0.16	a: 2.99, b: 1.91
BC_5@Au(110)	-0.24	a: 4.58, b: 1.35
BC_3@Ir(111)	-1.40	1.05
BC_5@Ir(111)	-1.17	2.76
BC_3@Ir(110)	-1.62	a: 0.03, b: 4.79
BC_5@Ir(110)	-0.39	a: 4.48, b: 2.07

III. The lattice parameters

Table S3. Lattice constants of BC_3, BC_5 and involved metal surfaces.

Structure	Lattice Parameters (Å)
BC_3	5.17
BC_5	4.40
BC_3-square	a=8.96 b=5.17
BC_5-square	a=7.62 b=4.40
Cu(111)	2.52
Ag(111)	2.88
Au(111)	2.90
Ir(111)	2.72
Cu(110)	a=357 b=254
Ag(110)	a=4.07 b=2.88
Au(110)	a=4.10 b=2.90
Ir(110)	a=3.84 b=2.71

IV. Supplementary figures of the thermodynamic phase diagram of BC_3 and BC_5 in vacuum and on distinct surfaces.

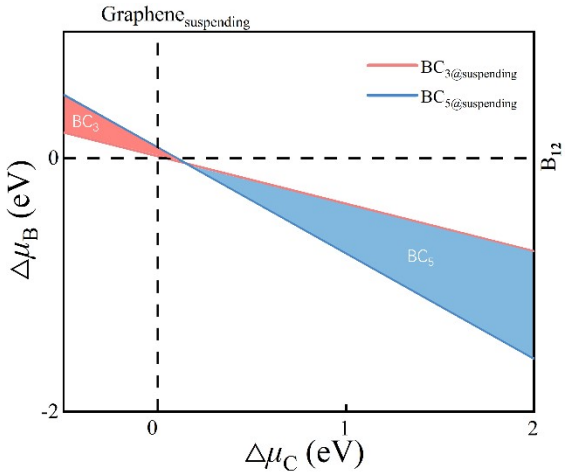

Figure S1. Thermodynamic phase diagrams of 2D B-G in vacuum. The chemical potential ranges which favor the formation of 2D B-G are painted in pink and blue, respectively. The horizontal and vertical dashed lines denote the chemical potential of suspended B_{12} molecules and graphene, respectively.

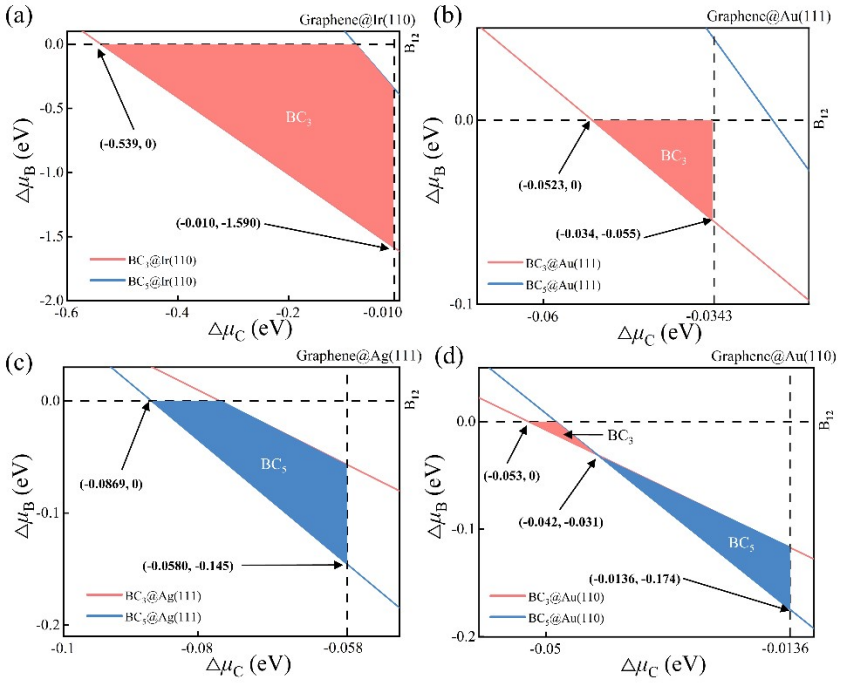

Figure S2. Thermodynamic phase diagrams of 2D B-G on two typical C_{2V} surfaces (a)Ir(110), (d)Au(110) and two C_{6V} surfaces (b)Au(111), (c)Ag(111). The chemical potential range for stable selective growth of 2D B-G are plotted. The coordinates of the intersection of the critical lines of distinct 2D B-G are denoted by arrows. The horizontal and vertical dashed lines signify B_{12} molecules and graphene on various substrates, respectively.

V. Optimized 2D B-G structure diagram on distinct surfaces

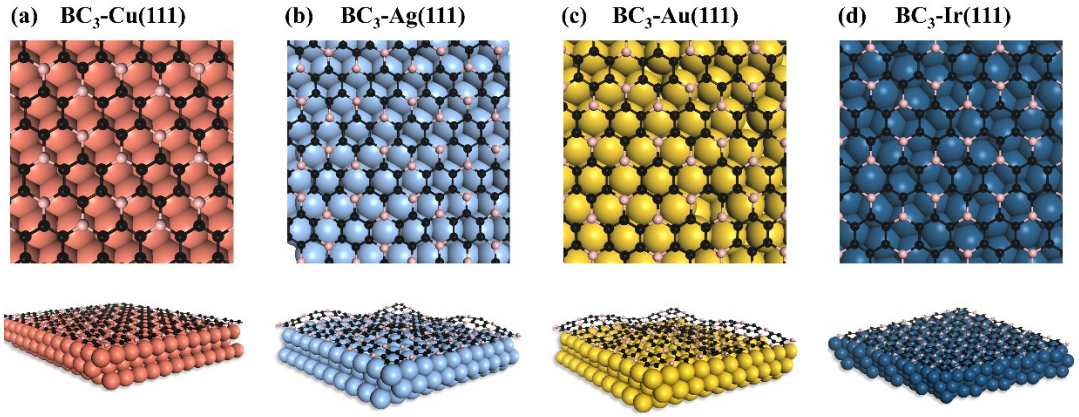

Figure S3. Top and perspective view of BC_3 on (a) Cu(111), (b) Ag(111), (c) Au(111), (d) Ir(111).

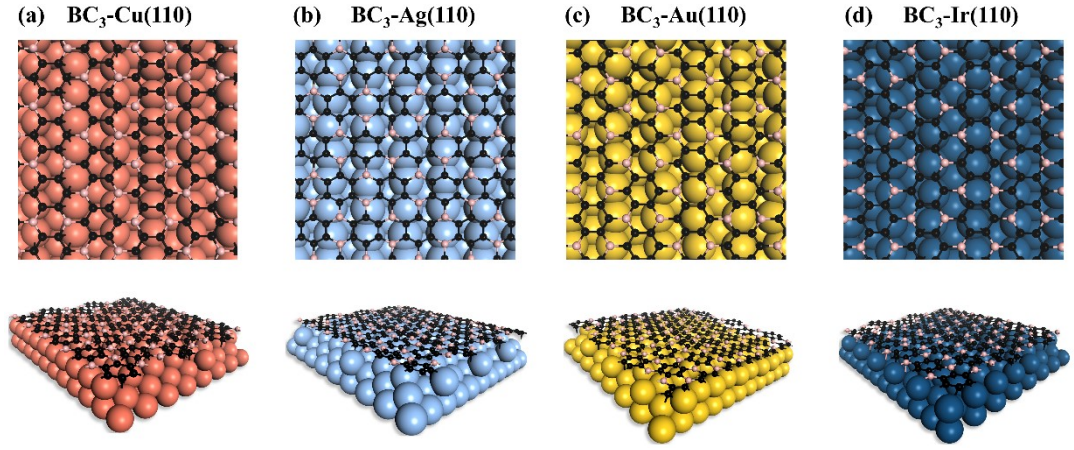

Figure S4. Top and perspective view of BC_3 on (a) Cu(110), (b) Ag(110), (c) Au(110), (d) Ir(110).

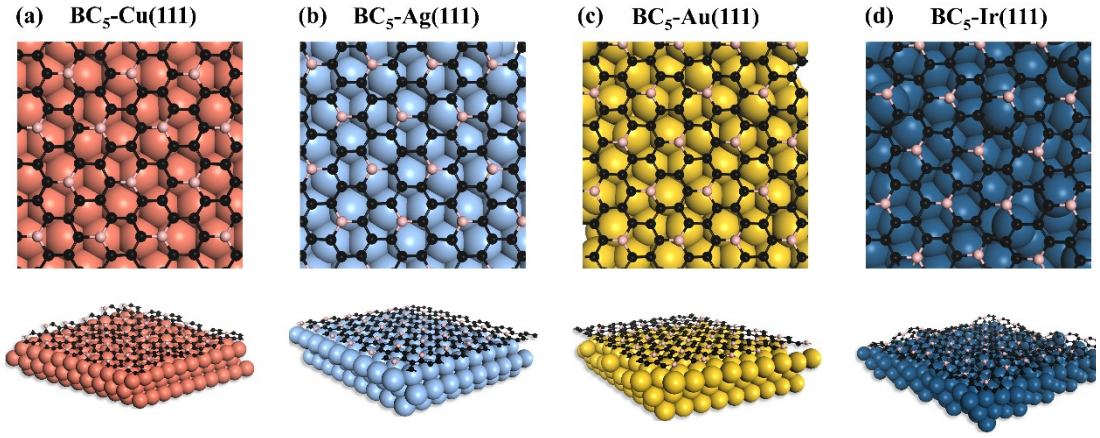

Figure S5. Top and perspective view of BC_5 on (a) Cu(111), (b) Ag(111), (c) Au(111), (d) Ir(111).

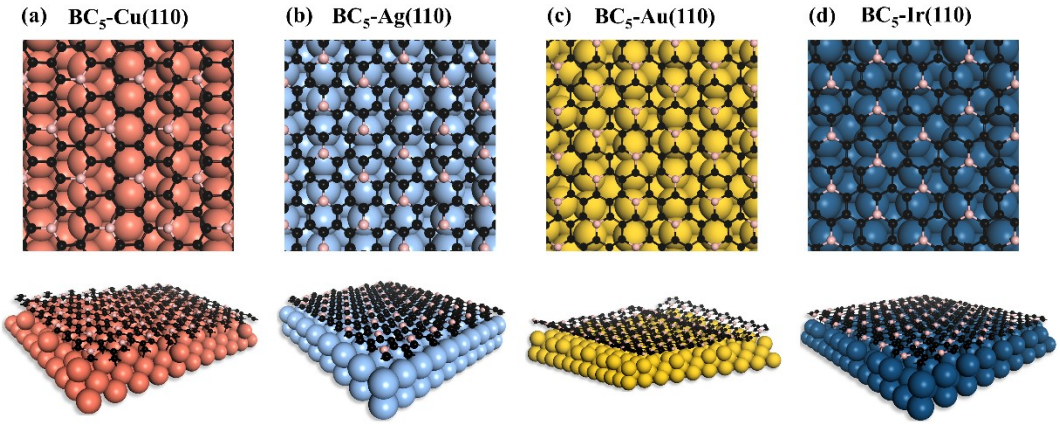

Figure S6. Top and perspective view of BC_5 on (a) Cu(110), (b) Ag(110), (c) Au(110), (d) Ir(110).