Supplementary Information

(1) Stability of random distribution configurations
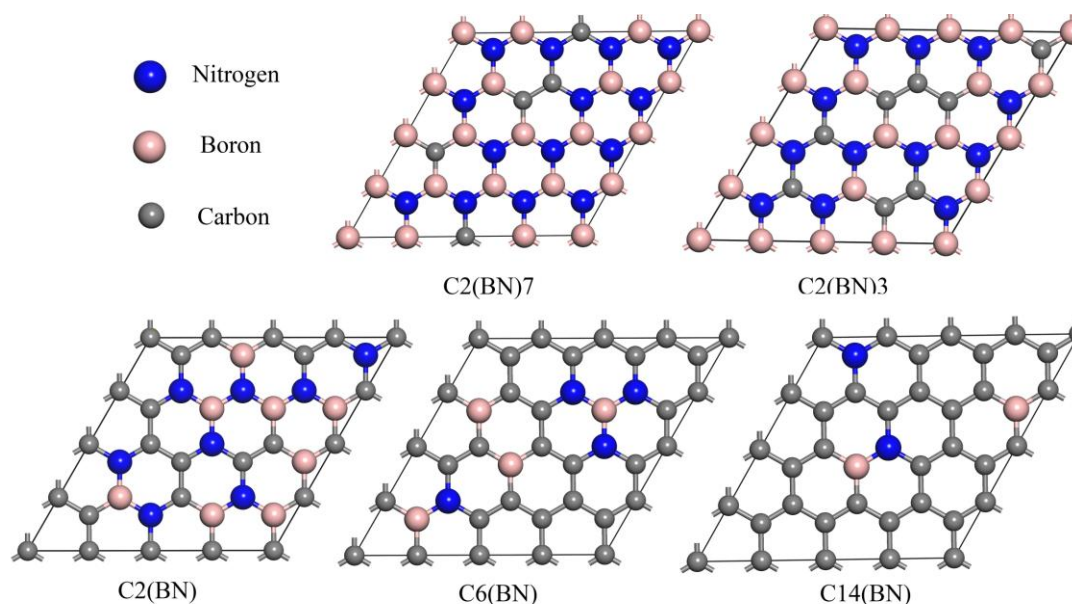

Figure S1 Structures with random distributions of B, N, and C species at different carbon contents.

The formation energies of systems can be expressed as functions of bond numbers,

$$\begin{cases} E_f = f(N_{C-N}, N_{C-B}, N_{B-N}, N_{C-C}, N_{B-B}, N_{N-N}) & \text{(S1)} \\ N_{total} = N_{C-N} + N_{C-B} + N_{B-N} + N_{C-C} + N_{B-B} + N_{N-N} & \text{(S2)} \end{cases}$$

where N_{X-X} is the number of X-X bond. For the computational models, the total bond number is determined. This constrain (Eq. (S2)) implies that the statistical weight of different bond type to the formation energy is different. Because the electrostatic attraction of B-N pair and the delocalized effect of C-C pair can significantly reduce the total energies of systems, the stable structures should have as many B-N and C-C bonds as possible. As the B-N and C-C bonds in random distribution structures are intermediate between the H and G structures, their formation energies are also expected to locate between H and G structures. Figure S2 confirms that the random distribution structures are less stable than the G(I) structures while they are more
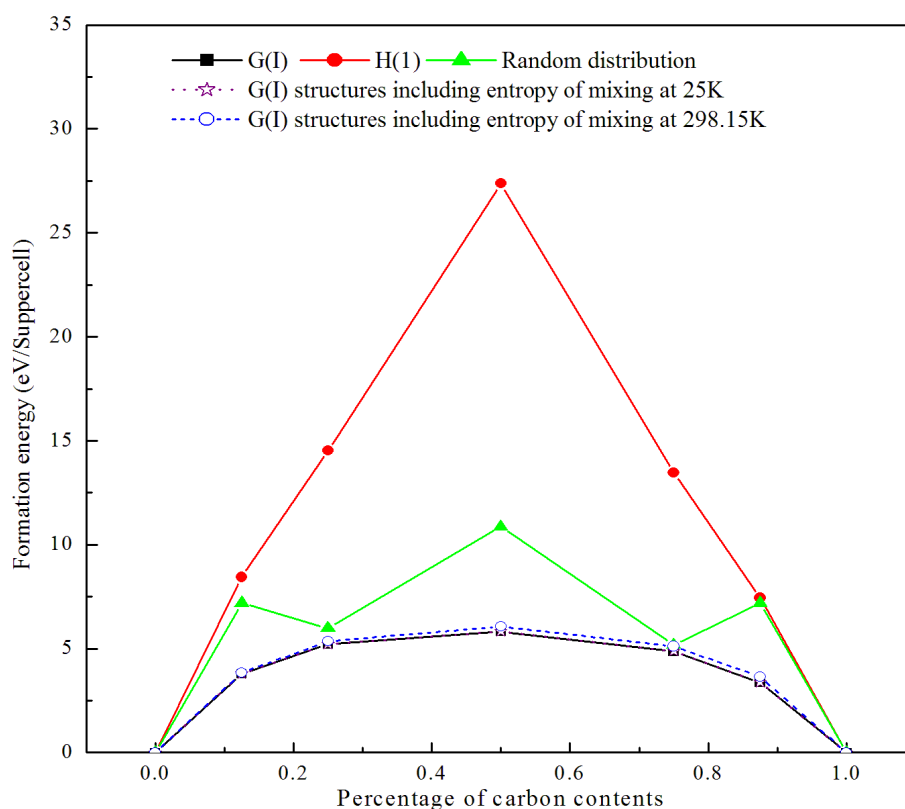
stable than H(I) ones indeed.

Figure S2 Formation energies of H(I), G (I), and random distribution configurations.

(2) Effect of entropy of mixing

To clarify the impact of entropy of mixing, Eq. (4) of the manuscript should be rewritten as follows,

$$G_f = G_{tot} - n_B G_{BN}^{sheet} - \frac{1}{2} n_C G_{CC}^{sheet}. \qquad (S3)$$

According to the definition of free energy ($G = E + PV - TS$), Eq. (S3) can be further expressed as

$$G_f = (E_{tot} - n_B E_{BN}^{sheet} - \frac{1}{2} n_C E_{CC}^{sheet}) - T(S_{tot} - n_B S_{BN}^{sheet} - \frac{1}{2} n_C S_{CC}^{sheet}) = E_f - T\Delta S \quad (S4)$$

where the *PV* term usually can be neglected for a solid material, and ΔS is the entropy of mixing. The calculated entropy of mixing is listed in Table S1 and also depicted in Figure S2. The result confirmed that the effect of entropy of mixing to the stabilities of systems is rather limited.

Table S1 Entropy (in Cal/mol·K) for G (I) structures

		Graphene	$C_{14}(BN)$	$C_6(BN)$	$C_2(BN)$	$C_2(BN)_3$	$C_2(BN)_7$	BN sheet
T = 25 K	Entropy	1.033	0.237	0.279	0.478	0.494	2.354	0.51
	$T\Delta S\,^a$	0.000	-0.017	-0.015	-0.013	-0.011	-0.007	0.000
T = 298.15 K	Entropy	4.098	41.317	41.621	38.729	42.443	47.116	3.122
	$T\Delta S\,^a$	0.000	-0.288	-0.259	-0.246	-0.148	-0.062	0.000

^{a} Entropy of mixing at a certain temperature (in eV/Supercell). ΔS was calculated according

to Eq. (S4)