Supplementary Material for **"Novel boron nitride polymorphs with graphite-diamond hybrid structure"**

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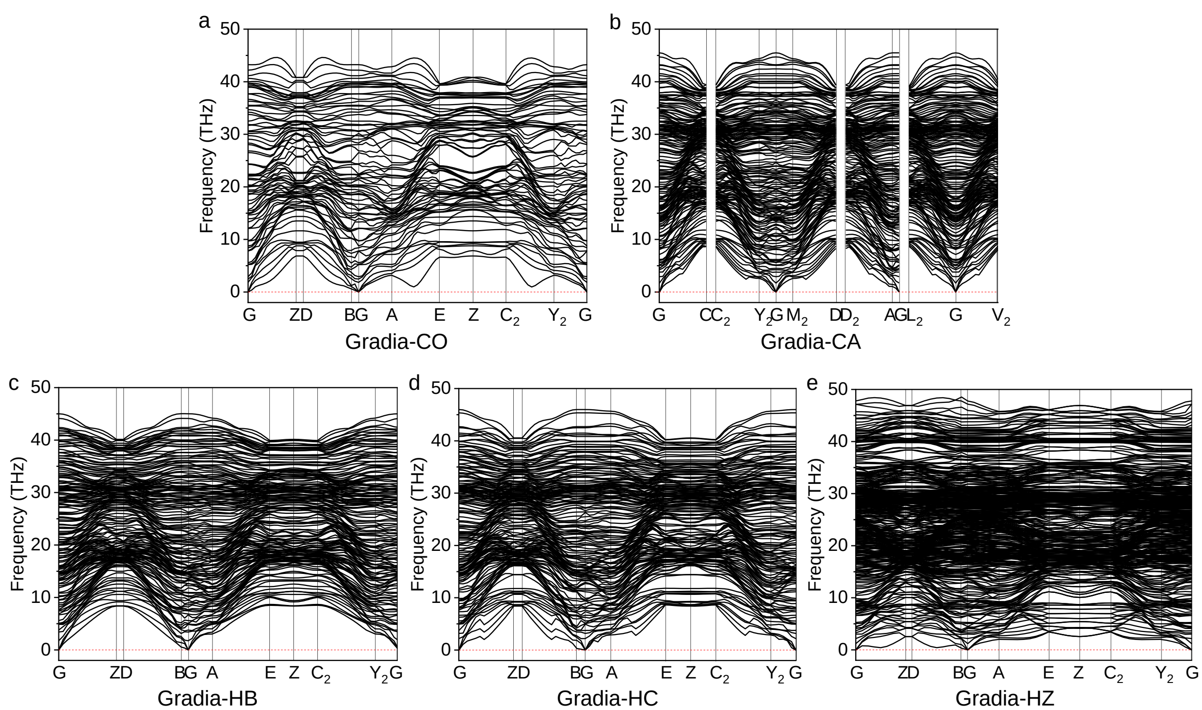

Fig. S1. Calculated phonon spectra of BN hybrid structures at ambient pressure. No imaginary phonon frequencies throughout the whole Brillouin zone indicates that all the structures are dynamically stable at ambient pressure.

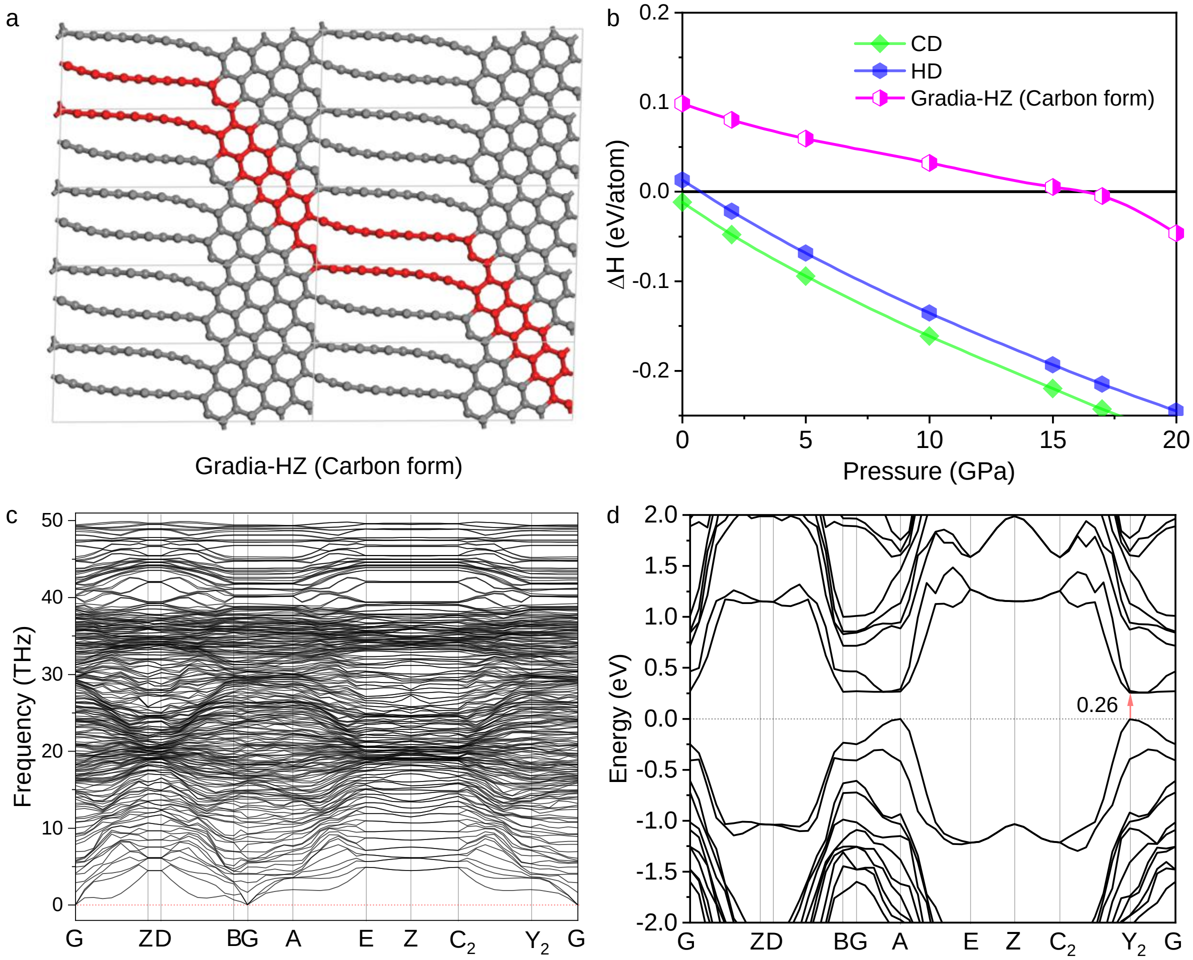

Fig. S2. Crystal structure, changes in enthalpy with pressure, ambient-pressure phonon spectrum and band structure of the Gradia-HZ in carbon form. (a) The representative periodic crystal structure of Gradia-HZ in carbon form, which was composed of graphite-like and HD units. The average interlayer spacing of the graphite-like layers in the hybrid structure was ~3.3 Å. The one-to-one correspondence between the graphite-like layer and HD unit is highlighted in red. (b) Changes in enthalpy of Gradia-HZ in carbon form with respect to graphite, as a function with pressure, showing that Gradia-HZ in carbon form was more stable than graphite above a pressure of 16 GPa. (c) Phonon spectrum of Gradia-HZ in carbon form calculated at ambient pressure. No imaginary phonon frequencies were observed throughout the whole Brillouin zone, which indicated that the Gradia-HZ in carbon form was dynamically stable. (d) Band structure of Gradia-HZ in carbon form, indicating that it was a semiconductor with a narrow bandgap of 0.26 eV.

Table S1. Space group (S.G.), lattice parameters (Å), and atomic Wyckoff positions of five BN hybrid structures and Gradia-HZ in carbon form optimized at ambient pressure.

Material	Structure type	S.G.	Lattice parameters	Atomic positions
BN	Gradia-CO	*Pm* (6)	*a* = 3.622 *b* = 2.516 *c* = 18.525 *β* = 91.731 °	B: 1*b* (0.252, 0.5, 0.648), 1*b* (0.269, 0.5, 0.925), 1*b* (0.257, 0.5, 0.787), 1*b* (0.772, 0.5, 0.280), 1*b* (0.395, 0.5, 0.482), 1*b* (0.216, 0.5, 0.071), 1*a* (0.807, 0, 0.984), 1*a* (0.763, 0, 0.855), 1*a* (0.069, 0, 0.383), 1*a* (0.765, 0, 0.577), 1*a* (0.754, 0, 0.718), 1*a* (0.491, 0, 0.176), N: 1*b* (0.980, 0.5, 0.587), 1*b* (0.999, 0.5, 0.722), 1*b* (0.581, 0.5, 0.209), 1*b* (0.002, 0.5, 0.000), 1*b* (0.008, 0.5, 0.859), 1*b* (0.172, 0.5, 0.414), 1*a* (0.512, 0, 0.928), 1*a* (0.493, 0, 0.652), 1*a* (0.504, 0, 0.790), 1*a* (0.867, 0, 0.313), 1*a* (0.305, 0, 0.104), 1*a* (0.523, 0, 0.510)
	Gradia-CA	*Cm* (8)	*a* = 2.515 *b* = 13.007 *c* = 20.542 *α* = 95.966 °	B: 2*a* (0.5, 0.469, 0.377), 2*a* (0.5, 0.619, 0.542), 2*a* (0.5, 0.262, 0.613), 2*a* (0.5, 0.365, 0.783), 2*a* (0.5, 0.486, 0.169), 2*a* (0.5, 0.444, 0.582), 2*a* (0.5, 0.818, 0.515), 2*a* (0.5, 0.715, 0.341), 2*a* (0.5, 0.192, 0.443), 2*a* (0.5, 0.979, 0.273), 2*a* (0.5, 0.651, 0.921), 2*a* (0.5, 0.545, 0.749), 2*a* (0.5, 0.210, 0.028), 2*a* (0.5, 0.007, 0.852), 2*a* (0.5, 0.903, 0.682), 2*a* (0.5, 0.953, 0.482), 2*a* (0.5, 0.734, 0.133), 2*a* (0.5, 0.466, 0.957), 2*a* (0.5, 0.232, 0.238), 2*a* (0.5, 0.988, 0.064), 2*a* (0.5, 0.825, 0.886), 2*a* (0.5, 0.724, 0.715), 2*a* (0.5, 0.185, 0.817), 2*a* (0.5, 0.084, 0.647), N: 2*a* (0.5, 0.354, 0.922), 2*a* (0.5, 0.489, 0.100), 2*a* (0.5, 0.987, 0.995), 2*a* (0.5, 0.237, 0.169), 2*a* (0.5, 0.501, 0.519), 2*a* (0.5, 0.610, 0.689), 2*a* (0.5, 0.966, 0.411), 2*a* (0.5, 0.146, 0.585), 2*a* (0.5, 0.250, 0.757), 2*a* (0.5, 0.180, 0.959), 2*a* (0.5, 0.476, 0.307), 2*a* (0.5, 0.692, 0.481), 2*a* (0.5, 0.985, 0.204), 2*a* (0.5, 0.208, 0.376), 2*a* (0.5, 0.329, 0.557), 2*a* (0.5, 0.429, 0.724), 2*a* (0.5, 0.969, 0.623), 2*a* (0.5, 0.070, 0.791), 2*a* (0.5, 0.724, 0.063), 2*a* (0.5, 0.533, 0.894), 2*a* (0.5, 0.892, 0.825), 2*a* (0.5, 0.787, 0.656), 2*a* (0.5, 0.728, 0.273), 2*a* (0.5, 0.711, 0.858)
	Gradia-HB	*Pm* (6)	*a* = 6.140 *b* = 2.511 *c* = 20.568 *β* = 95.683 °	B: 1*a* (0.334, 0, 0.237), 1*a* (0.530, 0, 0.044), 1*a* (0.106, 0, 0.425), 1*a* (0.828, 0, 0.236), 1*a* (0.710, 0, 0.440), 1*a* (0.001, 0, 0.037), 1*a* (0.443, 0, 0.892), 1*a* (0.279, 0, 0.720), 1*a* (0.707, 0, 0.573), 1*a* (0.300, 0, 0.598), 1*a* (0.854, 0, 0.867), 1*a* (0.875, 0, 0.745), 1*b* (0.257, 0.5, 0.336), 1*b* (0.010, 0.5, 0.522), 1*b* (0.410, 0.5, 0.138), 1*b* (0.925, 0.5, 0.137), 1*b* (0.437, 0.5, 0.508), 1*b* (0.735, 0.5, 0.335), 1*b* (0.161, 0.5, 0.818), 1*b* (0.991, 0.5, 0.646), 1*b* (0.566, 0.5, 0.794), 1*b* (0.588, 0.5, 0.671), 1*b* (0.152, 0.5, 0.941), 1*b* (0.727, 0.5, 0.964), N: 1*a* (0.436, 0, 0.106), 1*a* (0.697, 0, 0.922), 1*a* (0.282, 0, 0.304), 1*a* (0.765, 0, 0.302), 1*a* (0.958, 0, 0.105), 1*a* (0.545, 0, 0.626), 1*a* (0.714, 0, 0.798), 1*a* (0.140, 0, 0.651), 1*a* (0.558, 0, 0.500), 1*a* (0.971, 0, 0.480), 1*a* (0.281, 0, 0.942), 1*a* (0.119, 0, 0.774), 1*b* (0.356, 0.5, 0.205), 1*b* (0.172, 0.5, 0.400), 1*b* (0.598, 0.5, 0.020), 1*b* (0.859, 0.5, 0.203), 1*b* (0.000, 0.5, 1.000), 1*b* (0.687, 0.5, 0.402), 1*b* (0.260, 0.5, 0.553), 1*b* (0.427, 0.5, 0.725), 1*b* (0.998, 0.5, 0.872), 1*b* (0.407, 0.5, 0.847), 1*b* (0.853, 0.5, 0.577), 1*b* (0.832, 0.5, 0.700)
	Gradia-HC	*Pm* (6)	*a* = 6.050 *b* = 2.509 *c* = 21.164 *β* = 91.881 °	B: 1*a* (0.053, 0, 0.581), 1*a* (0.038, 0, 0.869), 1*a* (0.131, 0, 0.702), 1*a* (0.143, 0, 0.986), 1*a* (0.547, 0, 0.726), 1*a* (0.472, 0, 0.008), 1*a* (0.636, 0, 0.560), 1*a* (0.628, 0, 0.846), 1*a* (0.986, 0, 0.175), 1*a* (0.950, 0, 0.380), 1*a* (0.485, 0, 0.210), 1*a* (0.405, 0, 0.409), 1*b* (0.801, 0.5, 0.655), 1*b* (0.312, 0.5, 0.510), 1*b* (0.294, 0.5, 0.797), 1*b* (0.867, 0.5, 0.481), 1*b* (0.878, 0.5, 0.774), 1*b* (0.374, 0.5, 0.914), 1*b* (0.786, 0.5, 0.946), 1*b* (0.384, 0.5, 0.631), 1*b* (0.979, 0.5, 0.071), 1*b* (0.979, 0.5, 0.278), 1*b* (0.498, 0.5, 0.110), 1*b* (0.461, 0.5, 0.310), N: 1*a* (0.750, 0, 0.498), 1*a* (0.237, 0, 0.637), 1*a* (0.228, 0, 0.919), 1*a* (0.825, 0, 0.614), 1*a* (0.348, 0, 0.473), 1*a* (0.316, 0, 0.756), 1*a* (0.733, 0, 0.780), 1*a* (0.811, 0, 0.903), 1*a* (0.501, 0, 0.076), 1*a* (0.473, 0, 0.276), 1*a* (0.982, 0, 0.105), 1*a* (0.973, 0, 0.311), 1*b* (0.985, 0.5, 0.709), 1*b* (0.999, 0.5, 1.000), 1*b* (0.077, 0.5, 0.540), 1*b* (0.061, 0.5, 0.827), 1*b* (0.492, 0.5, 0.567), 1*b* (0.482, 0.5, 0.851), 1*b* (0.570, 0.5, 0.685), 1*b* (0.545, 0.5, 0.972), 1*b* (0.490, 0.5, 0.176), 1*b* (0.431, 0.5, 0.376), 1*b* (0.987, 0.5, 0.209), 1*b* (0.936, 0.5, 0.413)

Table S1. (continued)

Material	Structure type	S.G.	lattice parameters	Atomic positions
BN	Gradia-HZ	$P2_1$ (4)	a = 6.741 b = 4.244 c = 24.060 β = 93.670 °	B: 2*a* (0.243, 0.841, 0.711), 2*a* (0.245, 0.334, 0.661), 2*a* (0.223, 0.312, 0.768), 2*a* (0.242, 0.836, 0.608), 2*a* (0.656, 0.842, 0.750), 2*a* (0.241, 0.335, 0.556), 2*a* (0.401, 0.815, 0.197), 2*a* (0.307, 0.816, 0.092), 2*a* (0.154, 0.317, 0.046), 2*a* (0.038, 0.812, 0.160), 2*a* (0.249, 0.319, 0.150), 2*a* (0.328, 0.315, 0.873), 2*a* (0.707, 0.334, 0.702), 2*a* (0.882, 0.319, 0.114), 2*a* (0.941, 0.816, 0.057), 2*a* (0.518, 0.317, 0.081), 2*a* (0.611, 0.322, 0.185), 2*a* (0.577, 0.816, 0.023), 2*a* (0.788, 0.317, 0.011), 2*a* (0.949, 0.346, 0.208), 2*a* (0.760, 0.336, 0.496), 2*a* (0.757, 0.336, 0.600), 2*a* (0.258, 0.337, 0.349), 2*a* (0.239, 0.336, 0.452), N: 2*a* (0.750, 0.671, 0.288), 2*a* (0.758, 0.170, 0.340), 2*a* (0.775, 0.185, 0.232), 2*a* (0.757, 0.670, 0.392), 2*a* (0.349, 0.671, 0.250), 2*a* (0.758, 0.171, 0.444), 2*a* (0.599, 0.688, 0.803), 2*a* (0.693, 0.691, 0.908), 2*a* (0.847, 0.191, 0.954), 2*a* (0.961, 0.687, 0.839), 2*a* (0.751, 0.190, 0.851), 2*a* (0.672, 0.191, 0.127), 2*a* (0.286, 0.171, 0.297), 2*a* (0.118, 0.191, 0.887), 2*a* (0.058, 0.691, 0.943), 2*a* (0.482, 0.191, 0.920), 2*a* (0.388, 0.192, 0.816), 2*a* (0.423, 0.691, 0.977), 2*a* (0.212, 0.191, 0.989), 2*a* (0.036, 0.171, 0.788), 2*a* (0.240, 0.171, 0.504), 2*a* (0.242, 0.171, 0.400), 2*a* (0.743, 0.171, 0.652), 2*a* (0.761, 0.171, 0.548)
Carbon	Gradia-HZ	$P2_1/m$ (11)	a = 21.998 b = 4.182 c = 6.640 β = 88.249 °	C: 4*f* (0.788, 0.566, 0.157), 4*f* (0.807, 0.089, 0.946), 4*f* (0.616, 0.083, 0.216), 4*f* (0.672, 0.582, 0.205), 4*f* (0.561, 0.583, 0.227), 4*f* (0.505, 0.083, 0.240), 4*f* (0.768, 0.086, 0.591), 4*f* (0.716, 0.581, 0.651), 4*f* (0.662, 0.083, 0.698), 4*f* (0.394, 0.083, 0.272), 4*f* (0.449, 0.583, 0.253), 4*f* (0.273, 0.586, 0.805), 4*f* (0.162, 0.564, 0.696), 4*f* (0.024, 0.063, 0.069), 4*f* (0.099, 0.063, 0.776), 4*f* (0.085, 0.563, 0.991), 4*f* (0.174, 0.064, 0.481), 4*f* (0.123, 0.564, 0.345), 4*f* (0.988, 0.063, 0.716), 4*f* (0.062, 0.063, 0.423), 4*f* (0.050, 0.563, 0.638), 4*f* (0.865, 0.564, 0.869),

Table S2. Calculated elastic constants (C_{ij}, GPa) of the five BN hybrid structures and the Gradia-HZ in carbon form at ambient pressure.

C_{ij}	Gradia-CO (BN form)	Gradia-CA (BN form)	Gradia-HB (BN form)	Gradia-HC (BN form)	Gradia-HZ (BN form)	Gradia-HZ (Carbon form)
C_{11}	356.9	295.8	594.6	760.2	426.1	450.4
C_{22}	977.2	921.9	995.5	963.3	928.5	1181.5
C_{33}	434.3	521.8	484.3	434.0	744.6	926.6
C_{44}	544.6	286.0	200.4	192.6	333.2	451.7
C_{55}	184.0	209.8	151.1	34.4	27.3	67.1
C_{66}	139.9	232.6	320.1	353.2	143.2	186.6
C_{12}	124.1	66.3	120.5	135.6	29.1	14.0
C_{13}	169.4	251.7	146.7	120.5	74.2	107.8
C_{15}	-91.7	-13.9	224.0	-76.9	-25.4	-80.1
C_{23}	109.7	144.4	71.4	61.3	117.9	113.2
C_{25}	-53.1	67.7	33.1	-18.2	-13.3	11.2
C_{35}	-257.9	139.7	62.7	-7.2	-61.9	111.7
C_{46}	-244.8	105.5	65.9	-48.6	-28.3	22.6