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Design of a Class of New sp^2–sp^3 Carbons Constructed by Graphite and Diamond Building Blocks

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The sp^2–sp^3-hybridized carbon allotropes with the advantage of two hybrid structures possess rich and fascinating electronic and mechanical properties and they have received long-standing attention. We design a class of versatile sp^2–sp^3 carbons composed of graphite and diamond structural units with variable sizes. This class of sp^2–sp^3 carbons is energetically more favorable than graphite under high pressure, and their mechanical and dynamical stabilities are further confirmed at ambient pressure. The calculations of band structure and mechanical properties indicate that this class of sp^2–sp^3 carbons not only exhibits peculiar electronic characteristics adjusted from semiconducting to metallic nature but also presents excellent mechanical characteristics, such as superhigh hardness and high ductility. These sp^2–sp^3 carbons have desirable properties across a broad range of potential applications.

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Carbon is one of the most fascinating elements in nature because its chemical and physical properties are unlike any other element. The multiple chemical bonding possibilities (sp-, sp^2-, and sp^3-hybridized bonds) enable carbon to self-assemble into a large number of carbon allotropes[1–3] such as graphite, diamond, fullerene,[4] graphene,[5,6] nanotubes,[7] graphdiyne,[8,9] and amorphous carbon.[10] Among them, graphite and diamond are two classic carbon materials. Diamond is known as an ultrahard, brittle, and insulated material in nature determined by its sp^3 bonding, whereas layered graphite is a soft and conductive material with sp^2 hybridization. The carbon allotropes composed of both sp^2- and sp^3-hybridized bonds are expected to possess combined mechanical and electrical properties of graphite and diamond, which have received long-standing attention.[11–14]

One effective method to form sp^2–sp^3 carbons is through phase transition of sp^2 carbon under high pressure and high temperatures. For example, previous studies found that C_{60} fullerenes under pressure can transform into interesting sp^2–sp^3 1D, 2D, or 3D polymers, as well as some forms of amorphous carbons.[15–20] Glassy carbon is a disordered carbon allotrope consisting of sp^2-hybridized bonds; it can be transformed into various sp^2–sp^3 amorphous carbon forms with completely different mechanical, optical, and electrical properties in high-pressure experiments.[21–26] Moreover, the compression of carbon nanotubes (CNTs) yields exciting but intricate phases because of the complexity in diameters, lengths, and chirality of single- or multi-walled CNTs.[27–30] Therefore, various metastable sp^2–sp^3 carbons can be derived from distinct phase transitions of the sp^2 carbon precursors with different crystal structures under pressure due to kinetic factors.

These experimental results have inspired extensive theoretical research on novel sp^2–sp^3 hybrid carbon allotropes. Two techniques are commonly used to obtain new sp^2–sp^3 hybrid carbon structures. One is produced by the popular structural search software including CALYPSO,[31,32] USPEX,[33] AIRSS,[34] and CSA algorithm.[35] For instance, hex-C_{18}[36] and m-C_8[37] were predicted as 3D metallic carbon allotropes, whereas mC12, oC16, mC24, and oC24[38] were predicted as 3D superhard carbon allotropes. Moreover, superhard or ultrastrong 3D sp^2–sp^3 carbons with novel 1D and 2D conductivity were predicted.[39,40] The other is a bottom-up approach designed by self-assembling low-dimensional known carbon building blocks. For instance, T6 carbon[41] and T14 carbon[42] consisting of interlocking hexagons carbon, O-type and T-type carbon[43] consisting of interlocking diamond nanostripes, a series of sp^2–sp^3 hybrid 3D nanotube polymers,[44,45] and 3D graphene monoliths[46] reveal diverse electronic and mechanical properties.

Here, we design a class of sp^2–sp^3 graphite-diamond hybrid structures by self-assembling graphite and diamond units of different sizes as building blocks. Our first-principles calculations show that this class of

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carbon allotropes is thermodynamically, mechanically, and dynamically stable at ambient pressure. Moreover, these allotropes exhibit tunable electronic properties (from semiconductor to metal) and excellent mechanical properties (e.g., superhigh hardness and high ductility) by adjusting the sizes of graphite and diamond building blocks. All these merits make them promising materials that can be applied in a broad range of various fields.

We construct this type of sp^2–sp^3 graphite-diamond hybrid structure manually in the Materials Visualizer module of Materials Studio software.[47] After building these structures, the calculations are performed by using their primitive cell and based on density functional theory (DFT) as implemented in the CASTEP code.[48] The ultrasoft pseudopotential[49,50] is used, and the electron–electron exchange interaction is described by the exchange–correlation function of Ceperley and Alder, as parameterized by Perdew and Zunger of local density approximation.[51,52] A k-point sampling[53] of $0.03 \times 2\pi$ Å^{-1} and a plane-wave cutoff of 600 eV are used. Structural relaxation is stopped when the total energy change, the maximum ionic displacement, stress, and ionic Hellmann–Feynman force are less than 5.0×10^{-6} eV/atom, 5.0×10^{-4} Å, 0.02 GPa, and 0.01 eV/Å, respectively. The elastic constants are calculated in the linearly elastic strain range. The symmetry k-path in the Brillouin zone of primitive unit cells is determined by SeeK path[54] and used to calculate the phonon spectrum and band structure. The phonon spectra are calculated via the finite displacement method.[55] The selected calculation parameters are all tested to ensure that energy convergence is less than 1 meV/atom.[56–59] To validate our computational scheme, benchmark calculations are conducted for diamond. The calculated lattice parameters of $a = 3.53$ Å are in good agreement with the experimental results of $a = 3.57$ Å for diamond.[60] The calculated bulk modulus of diamond is 464.7 GPa, which is in agreement with the experimental data of 446 GPa.[60]

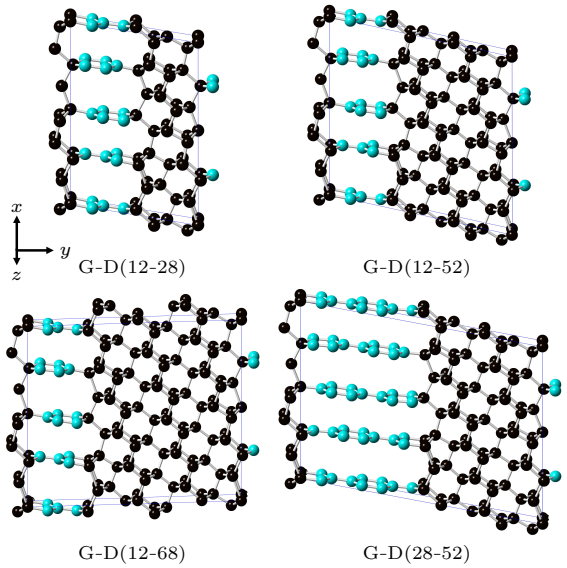

Fig. 1. Crystal structures of G-D(12–28), G-D(12–52), G-D(12–68), and G-D(28–52). The cyan spheres represent sp^2-hybridized carbon atoms, and the black spheres represent sp^3-hybridized carbon atoms.

Table 1. Space group (SG), lattice parameters (LP, Å), and atomic Wyckoff positions (all in 4i) of G-D carbons at ambient pressure.

Structure	SG	LP	Atomic positions
G-D(12–28)	$C2/m$ (12)	$a = 12.137$	(0.533, 0, 0.437) (0.368, 0, 0.151) (0.180, 0, 0.611) (0.306, 0, 0.650)
		$b = 2.481$	(0.636, 0, 0.012) (0.348, 0, 0.490) (0.137, 0, 0.267) (0.017, 0, 0.334)
		$c = 8.536$	(0.109, 0, 0.754) (0.142, 0, 0.096)
		$\beta = 99.525°$	
G-D(12–52)	$C2/m$ (12)	$a = 12.554$	(0.138, 0, 0.505) (0.350, 0, 0.323) (0.207, 0, 0.733) (0.127, 0, 0.395)
		$b = 2.487$	(0.601, 0, 0.331) (0.475, 0, 0.049) (0.179, 0, 0.063) (0.048, 0, 0.792)
		$c = 12.821$	(0.300, 0, 0.098) (0.832, 0, 0.164) (0.353, 0, 0.439) (0.131, 0, 0.164)
		$\beta = 102.754°$	(0.009, 0, 0.117) (0.473, 0, 0.276) (0.355, 0, 0.004) (0.665, 0, 0.234)
G-D(12–68)	$C2/m$ (12)	$a = 12.840$	(0.268, 0, 0.281) (0.025, 0, 0.740) (0.148, 0, 0.309) (0.216, 0, 0.777)
		$b = 2.517$	(0.148, 0, 0.006) (0.083, 0, 0.225) (0.136, 0, 0.496) (0.038, 0, 0.039)
		$c = 15.405$	(0.106, 0, 0.814) (0.335, 0, 0.050) (0.470, 0, 0.315) (0.369, 0, 0.550)
		$\beta = 91.760°$	(0.152, 0, 0.587) (0.357, 0, 0.361) (0.411, 0, 0.129) (0.521, 0, 0.094)
			(0.607, 0, 0.356) (0.599, 0, 0.171) (0.710, 0, 0.141) (0.226, 0, 0.085)
G-D(28–52)	$C2/m$ (12)	$a = 12.601$	(0.373, 0, 0.580) (0.109, 0, 0.296) (0.368, 0, 0.497) (0.827, 0, 0.122)
		$b = 2.479$	(0.142, 0, 0.629) (0.463, 0, 0.205) (0.588, 0, 0.248) (0.296, 0, 0.073)
		$c = 17.025$	(0.786, 0, 0.201) (0.355, 0, 0.003) (0.136, 0, 0.545) (0.121, 0, 0.378)
		$\beta = 101.042°$	(0.055, 0, 0.845) (0.344, 0, 0.242) (0.006, 0, 0.088) (0.658, 0, 0.176)
			(0.353, 0, 0.330) (0.126, 0, 0.123) (0.474, 0, 0.036) (0.177, 0, 0.048)

Figure 1 shows this class of sp^2–sp^3 graphite-diamond hybrid structures named G-D carbon. These G-D carbons exhibit monoclinic ($C2/m$) symmetry, regardless of how the size of graphite or diamond unit changes. On the basis of the numbers of sp^2 and sp^3 carbon atoms in a unit cell, we further name and distinguish them as G-D(12–28), G-D(12–52), G-D(12–68), and G-D(28–52), respectively. For example, G-

D(12–28) consists of 12 sp^2 and 28 sp^3 carbon atoms in the unit cell. The crystallographic information for optimized crystal structures of these four G-D carbons is listed in Table 1. In principle, the structures of G-D carbons can be adjusted due to the size change of graphite and diamond building blocks, resulting in fascinating and tunable properties for these G-D carbons.

To assess the stability of the proposed G-D carbons, we calculate their enthalpies, phonon spectra, and elastic constants. Figure 2 presents the enthalpies of G-D carbons relative to graphite in a pressure range of 0–35 GPa. At ambient pressure, these G-D carbons are metastable and have energies of 0.14–0.23 eV/atom higher than graphite. However, the G-D(12–68) and G-D(28–52) carbons are energetically more stable than the previously proposed M-carbon[61] and W-carbon[62] at ambient pressure. With the increase in pressure, these G-D carbons become more stable than graphite, indicating that they are pressure-induced phases and can be formed under pressure. Specifically, G-D(12–28), G-D(12–52), G-D(12–68), and G-D(28–52) have energies lower than graphite after 34, 17, 12, and 18 GPa, respectively. As the size of graphite or diamond units increases, the thermodynamic stabilities of G-D carbons are further enhanced and exceed those of T12-C,[63] Cco-C_8,[64] and C-carbon[65] and gradually approach the level of graphite or diamond. As the size of graphite units increases, the G-D carbons become closer to graphite. By contrast, the G-D carbons with a large size of diamond units have energies close to that of diamond. The unique atomic arrangements and favorable energies suggest that G-D carbons may be formed as an intermediate phase between graphite and diamond.

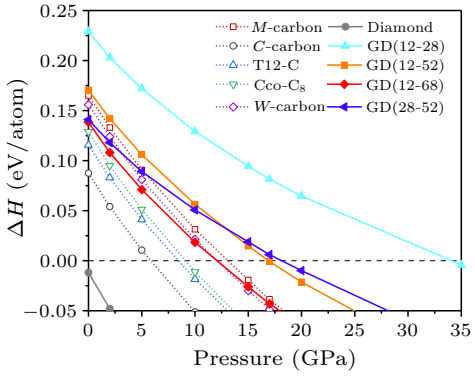

Fig. 2. Enthalpy of G-D(12–28), G-D(12–52), G-D(12–68), and G-D(28–52) as a function of pressure relative to graphite. Specifically, G-D(12–28), G-D(12–52), G-D(12–68), and G-D(28–52) have energies lower than graphite after 34, 17, 12, and 18 GPa, respectively.

Phonon analysis is further performed to determine the dynamic stability of these G-D carbons, as shown in Fig. 3. An imaginary frequency is absent in the phonon spectra of all G-D carbons throughout the entire Brillioun zone,[66] indicating their dynamical stability. The mechanical stability of our proposed G-D carbons is confirmed by calculating their zero-pressure elastic constants (Table 2). For a stable monoclinic structure, its 13 independent elastic constants C_{ij} should satisfy the well-known Born stability criteria.[67–70] The calculated elastic constants C_{ij} satisfy the mechanical stability criteria, confirming that G-D carbons are mechanically stable at ambient pressure.

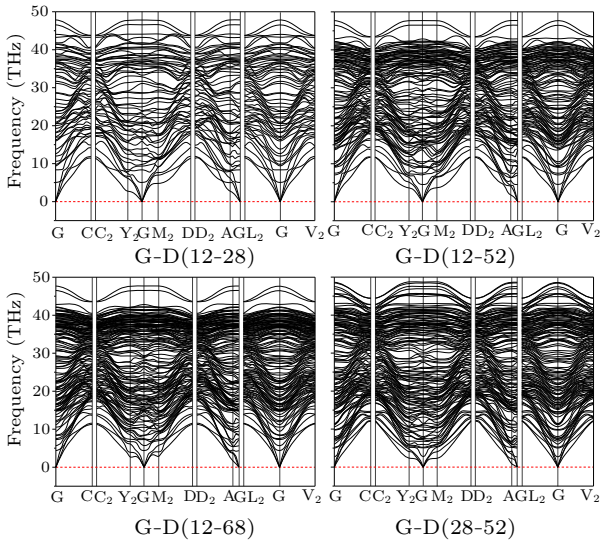

Fig. 3. Calculated phonon spectra of G-D(12–28), G-D(12–52), G-D(12–68), and G-D(28–52) at ambient pressure. There is no imaginary frequency in the phonon spectra of all G-D carbons throughout the entire Brillioun zone, indicating their dynamical stability.

Table 2. Calculated elastic constants (C_{ij}, GPa) of G-D(12–28), G-D(12–52), G-D(12–68), and G-D(28–52) at ambient pressure.

Phase	G-D(12–28)	G-D(12–52)	G-D(12–68)	G-D(28–52)
C_{11}	787.7	567.4	605.6	540.3
C_{22}	1163.3	1167.7	1174.6	1153.4
C_{33}	475.8	725.0	829.3	541.7
C_{44}	363.7	388.2	434.9	429.2
C_{55}	363.6	427.7	4024.7	348.0
C_{66}	398.7	448.4	436.4	308.9
C_{12}	95.0	92.9	73.8	52.4
C_{13}	318.9	369.5	333.4	353.1
C_{15}	164.6	80.0	−64.7	0.4
C_{23}	70.0	69.2	90.0	110.8
C_{25}	54.6	50.5	50.9	59.2
C_{35}	−31.6	48.8	130.8	238.8
C_{46}	98.5	76.4	75.7	102.5

Given the distinct sp^2 or sp^3 hybridization states, graphite is an excellent conductor, whereas diamond is an insulator with a wide bandgap of 5.5 eV. Novel electronic properties (Fig. 4) are expected in G-D carbons due to the hybridization of both sp^2 and sp^3 bonding types. Our calculations reveal that G-D(12–28), G-D(12–52), and G-D(12–68) are all semicon-

ductors with narrow direct bandgaps of 0.077, 0.108, and 0.118 eV, respectively. In comparison, G-D(28–52) shows a semimetallic nature. The bandgaps in G-D(12–28), G-D(12–52), and G-D(12–68) increase gradually with the increase in diamond units. The G-D carbons change their electronic properties along the line of semiconducting to semimetallic and to metallic nature with the increase in graphite units in the crystal structure. Compared with zero-bandgap graphene, this type of G-D carbons can show promising narrow-bandgap semiconductor properties through bandgap engineering by tailoring the structural elements of graphite and diamond inside. Thus, these materials have potential applications in electronic devices, such as transistors.

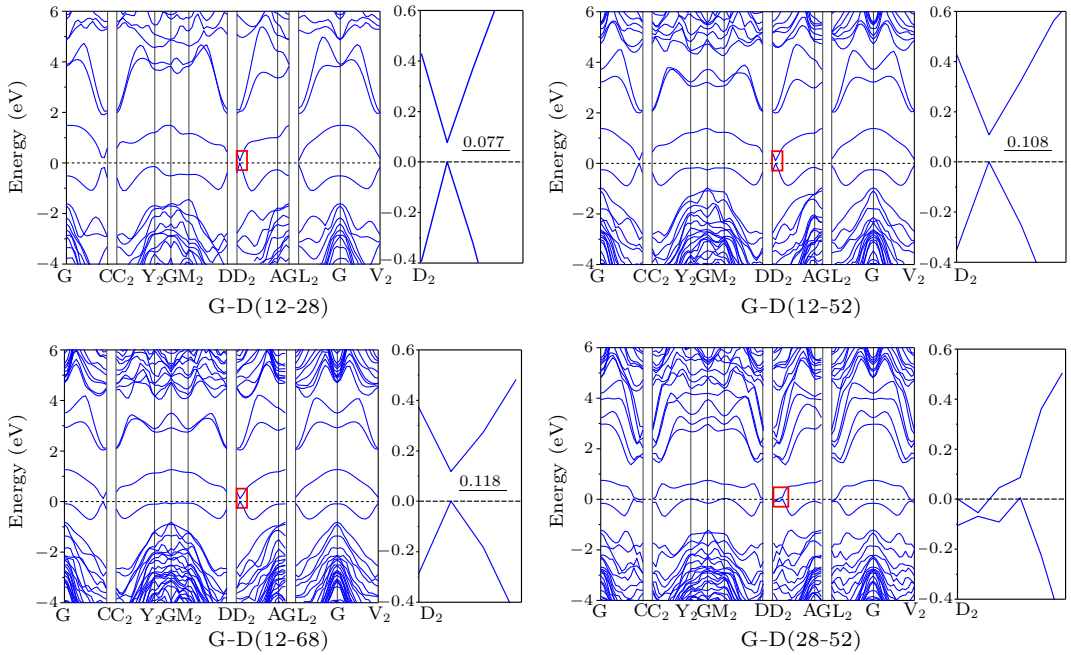

Fig. 4. Calculated band structures of G-D(12–28), G-D(12–52), G-D(12–68), and G-D(28–52) at ambient pressure. The intrinsic electronic characteristics of these G-D carbons are marked with red boxes and amplified to make them clearly visible.

Given their unique atomic arrangements and hybridization states, graphite and diamond have highly different mechanical properties: graphite is soft, whereas diamond is ultrahard and brittle. G-D carbons show a combination of the structural characteristics of graphite and diamond, so we expect that these carbons likely exhibit combined multifunctional mechanical properties, such as superhard nature and high ductility. Thus, we calculate the bulk moduli, shear moduli, Young's moduli, and Poisson's ratio for the currently designed G-D carbons (see Table 3). To ensure the accuracy of calculation, the moduli of graphite and diamond are first calculated, and the results are in good agreement with the experimental data.[71] The calculated bulk moduli, shear moduli, and Young's moduli of these four currently proposed G-D carbons are 306.7–387.3, 143.3–318.9, and 372–750.6 GPa, respectively, which are between those of graphite and diamond. On the basis of Chen's hardness model,[72,73] Vicker's hardness (H_v) values of G-D(12–28), G-D(12–52), G-D(12–68), and G-D(28–52) are 34.0, 39.7, 43.4, and 13.0 GPa, respectively. According to the generally accepted definition that a superhard material owns $H_v > 40$ GPa,[74] G-D(12–68) carbon can be regarded as a superhard material. Furthermore, it can be expected that the G-D carbons would have a hardness gradually approaching that of diamond as the size of diamond units increases in their structures.

Ductility is also important for the mechanical behavior of a material, and it describes the ability to deform without fracture. Low ductility or high brittleness can greatly affect the potential applications of carbon materials, even though they possess superhigh hardness. The brittleness and ductility can be qualitatively estimated by the B/G value in accordance with Pugh's rule,[75] and the critical value of B/G for ductile–brittle transition is 1.75. The four G-D carbons possess B/G ratios from 1.21 to 2.14, implying that their ductility is much better than diamond (0.85; Table 3). The ductility increase in G-D carbons is due to the flexible graphite building blocks inside, which can be deformed during stress. Increasing the size of the graphite building blocks can further improve the materials' ductility. Among the four G-D carbons, G-D(28–52) carbon exhibits the highest duc-

tility with $B/G = 2.14$, which is greater than the critical value of 1.75 or even more than the B/G values of 1.62,1.92, 2.07 for Zn, Ta, and Fe, respectively.[76] Therefore, these G-D carbons present superior comprehensive properties with superhard nature and high ductility, making them better than soft graphite and brittle diamond. These G-D carbons can meet the needs of a wide range of engineering fields.

Table 3. Bulk moduli (B), shear moduli (G), Young's moduli (E), Poisson's ratio (v), B/G ratio, and Vickers hardness (H_v) of G-D carbons at ambient pressure. The values in parentheses are the experimental data of diamond[43,60,77] and graphite[71] for comparison. All moduli are in unit of GPa, and v and B/G are dimensionless.

Carbon allotropes	B	G	E	v	B/G	H_v
Diamond	464.7 (446)	543.7 (527)	1173.4 (1133)	0.08 (0.07)	0.85 (0.84)	95.1 (60–120)
Graphite	36.3 (36.4)	10.9	29.8	0.36	3.33	1.3
G-D(12–28)	344.7	259.1	621.6	0.20	1.33	34.0
G-D(12–52)	373.5	296.2	702.9	0.19	1.26	39.7
G-D(12–68)	387.3	318.9	750.6	0.18	1.21	43.4
G-D(28–52)	306.7	143.3	372.0	0.30	2.14	13.0

In summary, a class of sp^2–sp^3 carbons named G-D carbons is designed by self-assembling graphite and diamond units as building blocks. First-principles calculations are performed to predict their electronic and mechanical properties. This class of G-D carbons achieves the required electronic and mechanical properties by adjusting the sizes of graphite and diamond building blocks. The G-D carbons are metastable at ambient pressure and become more stable than graphite under pressure. Their energies gradually approach that of graphite (or diamond) as the size of graphite (or diamond) units increases. Moreover, the band structures and elastic modulus calculations illustrate that the electronic properties of this type of G-D carbons are tunable from semiconductor to metal. They also demonstrate excellent combined mechanical performances, including superior ductility and superhigh hardness, by adjusting the sizes of graphite and diamond building blocks in structures. These G-D carbons may be used as an intermediate[78] to explain the mechanism of mutual transformation between graphite and diamond.[79–81] Our findings will stimulate further research interest in the experimental synthesis of this class of versatile sp^2–sp^3 carbons.

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