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Superhard and high-strength yne-diamond semimetals

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ABSTRACT

Two sp + sp^3-hybridized yne-diamond (YD) allotropes are designed by employing first-principle calculations. The YDs are constructed by replacing half carbon single bonds (C–C) along the <001> direction in 2H-diamond and 4H-diamond with acetylenic linkages (C–C≡C–C). Both YDs are energetically more favorable than experimental graphdiyne, theoretical graphynes (e.g., α-, β-, and 6,6,12-graphyne), and T-carbon. The YDs are confirmed to be mechanically and dynamically stable. Different from the recently proposed semiconductive YD based on cubic diamond (i.e. Y-carbon), electronic band structure calculations show that both YDs we proposed are semimetals. Mechanically, two YDs inherit the superhardness and high tensile strength from the parent diamonds. We hope that our present findings can be useful in guiding the design and syntheses of superhard and semimetallic carbon materials.

1. Introduction

Elemental carbon has never stopped surprising the world, and the development of new carbon materials has continued to foster breakthroughs in science and technology. Carbon adopts a wide range of allotropes because of its various hybridization states (sp^3, sp^2, and sp)—for instance, all sp^3-hybridized diamond polytypes, including cubic diamond, 2H-diamond, 4H-diamond, 9R-diamond, and so on; all sp^2-hybridized fullerenes, carbon nanotubes, graphene and graphite; all sp-hybridized carbyne; and sp^2 + sp^3-hybridized three dimensional polymers of nanotubes and fullerenes. The rapid growth of carbon allotropes has led to the current "era of carbon allotropes" which has provided an inexhaustible reservoir of carbon materials with versatile functionalities and that are utilized over a wide range of applications [1].

Considered as a guide for the synthesis of carbon materials, carbon allotropes that are specifically and theoretically designed to exhibit fascinating architectures, as well as impressive electronic and mechanical characteristics, have attracted wide attention [2–7]. In 1987, Baughman et al. theoretically assembled a novel type of carbon, called graphynes, by inserting acetylenic linkages (C–C≡C–C) into expanded graphite sheet (graphene) [8]. Given the diversities in site insertions, proportions, and lengths of acetylenic linkages, these sp + sp^2-hybridized carbons exist in various polymorphs, such as α-graphyne, β-graphyne, γ-graphyne [9], and graphdiyne [10]. Analogously, graphyne nanotubes [11,12] and fullereneynes [13,14] are constructed theoretically and projected to have low formation energies and excellent performance. Subsequently, graphdiyne, graphdiyne nanotubes, and graphyne molecular segment [15–17] are successfully confirmed in experiments. Inspired by sp + sp^2-hybridized carbon allotropes, sp + sp^3-hybridized yne-diamonds (YDs) are theoretically assembled by sticking acetylenic linkages into expanded cubic diamond [18–22] and the YD molecular segment (tetraethynylmethane) also has been obtained experimentally [23,24]. Recent calculations have indicated that acetylenic linkage is considerably stronger than the C–C bond, and Young's modulus of acetylenic rod is approximately 40 times larger than that of diamond [25] Therefore, YDs are expected to be a new kind of superhard material that can preserve the intrinsic properties of their parents [25]. However, recently constructed YDs are not as superhard as predicted, but instead turned out to be rather soft (H_v < 18 GPa) for the high proportion acetylenic linkages [19,21,25] and semiconductive with tunable band gaps (0.1 eV to 4.9 eV) [18,20,21]. Semimetallic and superhard YDs are full of expectation.

In this study, two YDs with hexagonal symmetry are predicted by employing first principle calculations. They are constructed via substituting half C–C bonds parallel to the <001> directions in 2H-diamond and 4H-diamond with C–C≡C–C linkages, and termed as 2HYD and 4HYD, respectively. Structurally, 2HYD and 4HYD can be viewed as the inter-layer jointed graphyne. Both YDs are energetically more favorable than experimentally synthesized graphdiyne and theoretical graphynes, such as α-graphyne, β-graphyne, and 6,6,6-12-graphyne, thereby strengthening their existence validities. Vibrational property analyses reveal that both carbons are dynamically stable at ambient conditions. Band structure calculations show that the two YDs are both semimetals, contrary to recently proposed semiconductive YDs and parent diamond. Mechanically, 2HYD and 4HYD are superhard

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materials that match certain properties of cubic boron nitride (c-BN) and inherit the high tensile strength from parent diamond.

2. Computational details

Structural relaxations and calculations of electronic properties were performed using density functional theory (DFT) within the local density approximation (LDA) as implemented in the Vienna Ab-initio Simulation Package (VASP) code [26]. The all-electron projector augmented wave (PAW) method was adopted with $2s^2 2p^2$ treated as valence electrons for carbon atom [27]. A plane-wave basis set with an energy cutoff of 660 eV was used and returned well-converged total energies. The Brillouin zone sample meshes based on the Monkhorst–Pack scheme [28] were set to be $24 \times 24 \times 8$ for both 2HYD and 4H-diamond, $24 \times 24 \times 4$ for 4HYD, $10 \times 10 \times 10$ for Y-carbon, $24 \times 24 \times 12$ for 2H-diamond, and $12 \times 12 \times 12$ for cubic diamond. To evaluate the dynamical stability, finite displacement method was used to calculate the phonon frequencies of metallic carbons based on the CASTEP code [29]. Primitive cells were used to calculate the elastic constants and Young's moduli by employing the CASTEP code.

3. Results and discussion

Recently, a YD, named Y-carbon (or so-called D-carbon), is constructed through inserting –C═C– linkages into all the C–C bonds in cubic diamond, resulting in large pore and low density [18–22]. It is known that the material mechanical strength is closely related to the pore structure of a material, and a larger pore usually brings in weaker strength [20]. Therefore, YDs with high density and small pore are explored. Here, two YDs, termed as 2HYD and 4HYD, are designed through replacing partial C–C bonds in 2H-diamond and 4H-diamond. The structural parameters, including space group, cell parameters, atomic positions, and densities are listed in Table 1. The space group of 2HYD is P-6*m*2, which is different from that of 2H-diamond. Carbon atoms located at 2 h(1/3, 2/3, 0.884) and 2i(2/3, 1/3, 0.195) constitute the sp^3-bonded diamond framework, and atoms at 1f(2/3, 1/3, 0.410) constitute the bridged acetylenic chains. As shown in Fig. 1(A), four kinds of covalent bonds exist in 2HYD carbon: I, sp-sp-hybridized triple bond; II, sp-sp^3-hybridized single bond; and III and IV, sp^3-sp^3-hybridized single bonds. The inserted acetylenic linkages significantly modify the bond lengths. The single bond IV, with a length of 1.537 Å, is unaffected because it is located far from the triple bond. The single bond III is stretched from 1.525 Å in 2H-diamond to 1.592 Å in 2HYD. The single bond II is 1.429 Å, which is close to that of graphene (1.420 Å). And the triple bond (C═C) I is 1.190 Å, approaching that of graphdiyne (1.22 Å). According to the bond length fluctuations, a single bond near the triple bond is strengthened, while that second far away from the triple bond is weakened. Acetylenic linkages maintain their straight conformation, while the sp^3-hybridized bonds lose their regular tetrahedron form, with bond angles ranging from 109.23° to 109.72°. Similar construction forms and bond changes are found in 4HYD carbon. The low percentage sp-hybridized carbon atoms in 2HYD and 4HYD account for their high densities (3.1 g/cm^3).

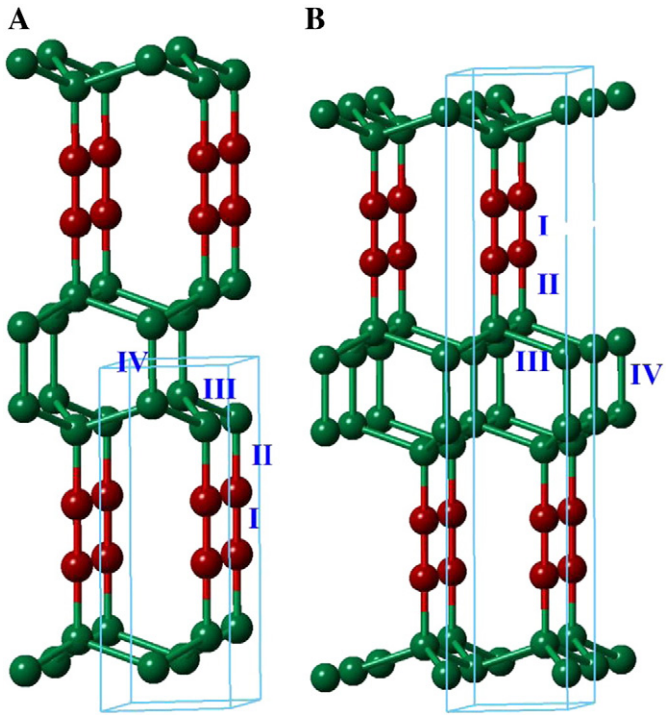

Fig. 1. Three-dimensional views of the yne-diamonds: (A) 2HYD and (B) 4HYD. Red and green spheres represent sp-hybridized and sp^3-hybridized carbon atoms, respectively. Symbol I represents triple bonds (C≡C), II represents single bonds (C–C) near triple bond, and III and IV represent single bonds far away from triple bond.

Structurally, 2HYD and 4HYD can be viewed as inter-layer bonded graphynes. It is well known that views along the *c*-axis of 2H-diamond and 4H-diamond are graphene. Similarly, two YDs present identical warped graphyne layers (termed as g-graphyne, which is formed by infinite strips of the hexagons interconnected by acetylenic linkages [30]) when viewed from the *a*-axis in 2HYD or from the *b*-axis in 4HYD (Fig. 2). The downside two plates in Fig. 2 describe the layer wrinkling and bonding models of 2HYD and 4HYD, similar to the

Table 1
Space group (S.G.), cell parameters (Å), atomic Wyckoff positions, and density (g/cm^3) of diamond polytypes and YDs.

Structure	S.G.	Cell parameters	Atomic positions	ρ
2H-diamond	P63/*mmc* (194)	a = 2.484 c = 4.137	4*f* (1/3, 2/3, 0.063)	3.6
4H-dimaond	P63/*mmc* (194)	a = 2.490 c = 8.216	4*f* (1/3, 2/3, 0.156) 4*e* (0, 0, 0.407)	3.6
cubic diamond	F*d*-3*m* (227)	3.533	8*b* (−1/4, 1/4, 1/4)	3.6
2HYD	P-6*m*2 (187)	a = 2.603 c = 6.634	2*h* (1/3, 2/3, 0.884) 2*i* (2/3, 1/3, 0.195) 1*f* (2/3, 1/3, 0.410)	3.1
4HYD	P63/*mmc* (194)	a = 2.608 c = 13.215	4*f* (1/3, 2/3, 0.097) 4*f* (2/3, 1/3, 0.705) 4*e* (0, 0, 0.443)	3.1
Y-carbon	F*d*-3*m* (227)	a = 9.540 a = 9.636[18] a = 9.512/9.529[19] a = 9.8829[20]	8*a* (0, 0, 0); 32*e* (0.089, 0.089, 0.089)	0.9