Multithreaded Conductive Carbon: 1D Conduction in 3D Carbon

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Abstract: Carbon possesses various allotropes with diverse electronic properties from insulation to conduction due to the sp , sp^2 , and sp^3 bonding types. Here, a new sp^2 - sp^3 carbon allotrope, called C_{48} , is proposed. C_{48} presents a lilac-like structure with a cage-like center and four petal-like tubes around, and can be formed through compressing single-walled carbon nanotubes. C_{48} is not only strong and hard in 3D but also has unexpected 1D conduction along eight divided linear pathways in the unit cell. This multithreaded 1D conduction in 3D framework is peculiar in carbon materials, and would be helpful to design singular electronic nanodevices.

1. Introduction

Elemental carbon fosters various polymorphs, such as graphite, diamond, graphene, and carbon nanotubes (CNTs), due to the ability to form sp , sp^2 , and sp^3 bonds. The carbon allotropes with different bond types reveal distinct electronic properties. Generally, all- sp^3 carbons including diamond and theoretical M-carbon[1], bct-C₄[2, 3], W-carbon[4], and Cco-C₈[5] are semiconductors because all valence electrons are tightly localized in the covalent bonds. As an exception, Tri-carbon with bent sp^3 bonds shows metallicity contributed to the extremely anisotropic bonds featuring π state characteristics[6]. On the other hand, most of the theoretical metallic carbons, such as K4-carbon[7], T6-carbon, T14-carbon[8], and some 3D CNT polymers[9], are all- sp^2 or sp^2 - sp^3 hybridized with conductivity originated from the delocalized electrons of sp^2 atoms similar to that of graphite, graphene and CNTs. By manipulating the location of sp^2 and sp^3 atoms, the 3D carbons with controllable conduction can be designed expectedly, and the deeper thinking about their formation need to be worthy of attention.

As is well-known, pressure-induced changes of bonding from sp^2 to sp^3 for sp^2 -hybridized carbons such as graphite, fullerenes, and CNTs are the key for producing new carbon phases with novel ~~electronic~~ **electrical** properties and superior mechanical performance. Due to the difference of crystal structures and hybridized forms of raw carbons, these carbon precursors would undergo distinct phase transitions under pressure due to the kinetic factor. Recently, transition behavior of zigzag (n , 0) and armchair (n , n) single-walled carbon nanotubes (SWCNTs) under hydrostatic and

nonhydrostatic pressures were systematically studied. Some new carbons were revealed such as 3D (2, 2)-II (Bct-C₄[10]), 3D (2, 2)-III (Cco-C₈[5]), 3D (3, 3)-I[11], 3D (5, 0)-III[12], 3D (6, 0)-I[13], 3D (7, 0)[12], and 3D (8, 8) carbon[13]. Among them, all- sp^3 carbons would be readily formed by compressing SWCNTs with relatively small ~~diameter~~ **diameters**[5]. Meanwhile, mixed sp^2 - sp^3 hybridized carbons were usually obtained from compressing large-diameter SWCNTs[12, 13]. Considering these sp^2 - sp^3 carbons commonly possess the 3D conductivity, it is highly desirable to search new 3D carbons displaying peculiar 1D or 2D electronic properties, **which would be attractive to be** applied in **specific**-~~specified~~-~~conduction~~ of nano-electronic devices.

In this study, a sp^2 - sp^3 3D carbon, called C₄₈, with novel 1D multithreaded ~~conductivity~~ **conduction** is proposed. The C₄₈ has a charming lilac-like structure with a cage-like center composed of sp^3 bonds as well as four ~~surrounding~~ **surrounded** petal-like tubes of both sp^2 and sp^3 hybridizations. The sp^2 atoms are specifically located at the divided area, endowing the multithreaded linear ~~conductivity~~ **conduction**. Due to the intervention of sp^3 atoms, the mechanical properties such as strength, hardness, and modulus have been improved in comparison with ~~that~~ **those** of pure sp^2 carbons. Furthermore, the C₄₈ has also been proved to be formed by direct compression of large-diameter (12, 12) SWCNT bundle, demonstrating its viability. The multithreaded 1D conduction in 3D carbon framework has the conductive behavior distinct from 3D ~~conductivity~~ **conduction** of graphite and 2D ~~conductivity~~ **conduction** of Dirac graphene, presenting the great potential of carbon materials.

2. Calculation methods

To obtain the reasonable sp^2 - sp^3 carbon configurations, the raw bundles of SWCNTs with tube diameter as large as 1.627 nm and intertube distance of 0.34 nm were built through the Materials Studio software, and then they were compressed at different pressures. Structural relaxations and property calculations were performed based on the density functional theory (DFT) as implemented in the CASTEP code[14]. The Vanderbilt ultrasoft pseudopotential was used and the electron-electron exchange interaction was described by the exchange-correlation function of Ceperley and Alder, as parameterized by Perdew and Zunger (CA-PZ) of the local-density approximation (LDA)[15, 16]. The plane-wave cutoff energy was 310 eV, and a k -point spacing ($2\pi \times 0.04 \text{ \AA}^{-1}$) was used to generate Monkhorst-Pack k -points grids for Brillouin zone sampling[17]. The finite displacement method was used to calculate the phonon frequencies of C_{48} . The unit cells were chosen to calculate the band structures, bulk modulus, shear modulus and elastic constants. The Vickers hardness was estimated using Chen's hardness model[18, 19].

3. Results and discussion

The designed C_{48} has a tetragonal structure (space group: $P4/mmm$, No.123) with 48 atoms per unit cell. Fig. 1 shows a perspective view of C_{48} with a cage-like center surrounded by four squashed tubes, and the optimized lattice parameters and Wyckoff atomic positions at ambient pressure are also listed. There are six kinds of nonequivalent carbon atoms in the unit cell including two kinds of sp^2 gray atoms

separated by other sp^3 black atoms. The sp^2 gray atoms are linearly connected along z axis, but are disconnected in the x - y plane. The bond angle of sp^2 atoms is not the perfect 120° but 122.02° due to the bond bending. The thermodynamic stability of C_{48} is ~~compared~~ comparable with those of experimental and theoretical carbon allotropes. The C_{48} has an ambient-pressure enthalpy of 0.43eV/atom higher than that of graphite, and thereby is metastable relative to graphite, diamond, and large-diameter SWCNTs at ambient pressure. However In spite of this, C_{48} has a similar enthalpy with that of fullerene C_{60} , and is more stable than some theoretically proposed sp^2 - sp^3 compressed SWCNT structures like 3D (3, 3)-I[11], 3D (6, 6)-I[13], and 3D (8, 8)[13], indicating its viability.

Figure 1. The crystal structure of C_{48} (a) and its side views along the $[100]$ (b) and $[110]$ (c) directions, respectively. The sp^2 and sp^3 hybridized atoms are colored as gray and black. The C_{48} has a space group of $P4/mmm$ with ambient-pressure lattice parameters of $a=12.35\text{ \AA}$, $c=2.47\text{ \AA}$, and Wyckoff atomic positions of $8q$ (0.153, 0.939, 0.5), $8q$ (0.356, 0.189, 0.5), $8q$ (0.436, 0.277, 0.5), $8p$ (0.204, 0.110, 0), $8p$ (0.435, 0.349, 0), and $8p$ (0.313, 0.153, 0).

Guaranteeing structurally the mechanical stability of structure is essential before property predictions. The calculated elastic constants of C_{48} are $C_{11}=382.15$, $C_{33}=963.16$, $C_{44}=247.54$, $C_{66}=141.52$, $C_{12}=259.68$, and $C_{13}=48.25\text{ GPa}$, respectively,

which meet the mechanical stability criteria for a tetragonal phase, i.e. $C_{11}>0$, $C_{33}>0$, $C_{44}>0$, $C_{66}>0$, $C_{11}>C_{12}$, $C_{11}+C_{33}>2C_{13}$, $(2C_{11}+2C_{12}+C_{33}+4C_{13})>0$ [20]. As a result, the C_{48} is mechanically stable. The bulk (B) and shear (G) moduli of C_{48} are 264.70 and 182.63 GPa, respectively. The B/G ratio[21] and Poisson's ratio[22] of C_{48} are 1.45 and 0.22, respectively. Both of them are higher than that of diamond (0.82 and 0.07) and cubic BN (0.97 and 0.12), indicating it is more ductile than the two superhard materials. The **ambient-pressure** phonon dispersion curves ~~at ambient pressure was~~ **were** simulated ~~to determine the dynamic stability,~~ and no imaginary frequency ~~is~~ **was** detected throughout the whole Brillouin zone (Fig.2b), demonstrating the dynamic stability of C_{48} . Therefore, the C_{48} is thermodynamically, mechanically, and dynamically stable, and can be theoretically quenched to ambient pressure.

Figure 2. Ambient-pressure electronic band structure (a) and phonon dispersion curves (b) of C_{48} .

To explore the potential unique ~~electric~~ **electrical** properties, we calculated the electronic band structure (Fig.2a), and overall it shows that C_{48} is a conductor. Seen from the band structure, several flat bands crossed Z and R points as well as Z and A

points appear at the Fermi level. Meanwhile, some steep conduction bands along M and G points toward to A or Z point as well as Z and R points toward to G or X point are observed to pass through the Fermi level repeatedly. The contemporary existence of flat and steep bands at the Fermi level can be regarded as a “fingerprint” for a superconducting compound[23], indicating the possible superconductivity of C₄₈.

In order to figure out the conductive mechanism, we further calculated the electronic partial density of states (PDOS), ~~and~~ electron localization functions (ELF) ~~and electron~~ ~~orbits~~ of C₄₈ (Fig.3). Seen from the PDOS (Fig.3a), the conductive electrons are almost from the atoms at C3 and C4 positions, which are corresponding to the sp^2 atoms marked as green and red ones, respectively. Other sp^3 atoms in structure have no contribution to the conductivity due to the saturation of chemical bonds. Because the sp^2 atoms are linearly linked each other along z axis, it is easy to conclude their z-axis conductivity. However, the key is to understand the electron coupling between sp^2 layers in order to judge the electrical ~~conductivity~~ behavior in x-y plane. As is well-known, ELF is ~~used to identify the electron correlation~~ ~~useful to provide the~~ ~~bonding information~~. The values of ELF can be ranged from 0.0 to 1.0, where 1.0 is corresponding to perfect localization, and 0.5 is corresponding to perfect electron delocalization. To analyze the bonding state between the sp^2 interlayers in structure, we draw out the ~~electronic~~ isosurface map of ELF=0.5 (Fig.3b). ~~Clearly, there are no electron density between the sp^2 interlayers, indicating the perfect electron delocalization.~~ Clearly, there is a gap of electron localization between the sp^2

interlayers, indicating the insulated interlayers. In addition, this gap is independent on the choice of isosurface value of ELF.

To further demonstrate the delocalized π electrons and elucidate the conduction behavior of the sp^2 carbon chains along z axis, we have calculated the electron orbits of C_{48} originated from the bands across the Fermi level (Fig.3c and 3d). Clearly, the π electrons attached in the sp^2 carbon chains are separated in x - y plane (Fig. 3d) but linked each other along z axis (left in Fig.3c). Therefore, the eight divided sp^2 regions of unit cell are not conductive in x - y plane, but only linearly conductive along z axis. Furthermore, our calculation also shows that the electron orbits of sp^3 carbon atoms are all localized and separated in x - y plane (Fig.3d) and z axis (right in Fig.3c), thereby leading to their insulation in 3D. In short, the analyses of PDOS, ELF, and electron orbits support the consistent result that the C_{48} is a 3D carbon with peculiar 1D multithreaded conductivity. ~~In short, the C_{48} is a 3D carbon with peculiar 1D multithreaded conductivity.~~

Figure 3. (a) PDOS of C₄₈. The inset is the crystal structure of C₄₈ with six nonequivalent atomic positions marked by different colors corresponding to those in PDOS. Only the atoms located in C3 and C4 positions contribute to the conductivity. (b) ELF of C₄₈ at isosurface equal to 0.5 representing the perfect electron delocalization. Clearly, there is no electron density between the sp^2 interlayers, resulting in the eight divided linear conductive paths composed of C3 and C4 atoms along z axis. Clearly, there is a gap of electron localization between the sp^2 interlayers, indicating the interlayers are non-conductive. (c), (d) Electron orbits of C₄₈ originated from the bands across the Fermi level. The selected isosurface is 0.0115. The electron orbits are all insulated in x - y plane (Fig. 3d), and the π bonds attached in the sp^2 carbon chains are linked each other along z axis, resulting in the linear conductivity (left in Fig. 3c). In comparison, the localized electron orbits of the sp^3 carbon atoms are still divided along z axis, leading to their insulation in 3D (right in Fig. 3c).

The axial (z axis) and radial tensile strengths of C₄₈ were further calculated. As shown in Fig.4, the tensile strengths along the [001], [100] and [110] directions are

109.12 GPa with a strain of 0.25, 45.36 GPa with a strain of 0.22, and 26.04 GPa with a strain of 0.08, respectively. The axial [001] tensile strength of C_{48} is about double that of current calculated (12, 12) SWCNTs, and is comparable with the in-plane intrinsic tensile strength of graphene reaching 130 ± 10 GPa[24]. Its radial tensile strength has been greatly improved, far higher than those of 1D carbon nanotubes and nanowires with weak Van der Waals force. The lowest tensile strength is along the [110] direction and the crystal would be cleaved along the [110] direction when the external stress exceeds 26.04 GPa. ~~Notely~~ **Notably**, the re-enhancement along the [100] direction was observed during tension, and this is due to the successive bond destruction originated from C2 atoms and C1 atoms. In addition, the Vickers hardness is also estimated by Chen's hardness model[18, 19], and the C_{48} has a hardness of 24.26 GPa, implying that it is a hard material.

Figure 4. Calculated tensile strengths versus tensile strains of C_{48} along the [001], [100], and [110] orientations, respectively. In comparison, the strongest crystal orientation of (12, 12) SWCNTs is marked by [001].

We further provide the possible formation of C_{48} through compressing (12, 12) SWCNT bundle under hydrostatic pressure of 60 GPa (Fig.5). Firstly, the rounded tubes in array were compressed into flat squares (Fig.5b). Further compression led to the formation of a screw-propeller-like polymer linked by the sp^3 C–C bonds at the corners (the green sticks, Fig.5c). Finally, the tubes were contracted and new sp^3 bonds at inner tube were formed to construct the crystal structure of C_{48} (Fig.5d). Recently, the growth of SWCNTs with specific chirality has attracted lots of research groups' attention, ~~and now~~. The production of (12, 12) SWCNTs has been reported before, but the product has a low purity and also includes other chiral nanotubes[25-27]. Now high-yield production of (12, 6) SWCNTs with single chirality has been successfully achieved[28]. The large-scale synthesis of other high-purity SWCNTs with controllable chiralities is highly anticipated in near future, and then the predicted SWCNTs polymers including C_{48} may be easily synthesized.

Figure 5. Formation of 3D C₄₈ by compressing 1D (12, 12) SWCNTs **under hydrostatic pressure of 60 GPa**. (a) Original nanotube array. During compression, the nanotubes are squashed into race track-like shape (b). Further compression induces the intertube (c) and intratube (d) bonding, and finally to form C₄₈ (d). The green sticks represent the new sp^3 bonds during compression, and the region including red lines represents the unit cell of C₄₈.

4. Conclusions

In sum, a novel sp^2 - sp^3 hybridized carbon, i.e. C₄₈, with a fascinating lilac-like structure has been proved to be mechanically and dynamically stable, and would be formed during compressing the large-diameter SWCNTs. Structurally, C₄₈ has a tetragonal unit cell containing a sp^3 cage-like center surrounded by four sp^2 - sp^3 petal-like tube configurations. The electron analysis shows that C₄₈ has eight separated atom-scaled linear conductive channels in the unit cell, making it having 1D multithreaded

conduction in 3D. This conducting behavior is distinct from the 1D conduction of 1D SWCNTs, 2D conduction of 2D graphene, and also 3D conduction of 3D graphite, which is unique in carbon materials. The 1D multithreaded conductive channels can allow straight and adjustable electron transports, and the 3D sp^2 - sp^3 framework would support the excellent mechanical properties such as strength, moduli, and hardness, making C_{48} find potential application in various electronic nanodevices like field emission devices.

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