

Carboneyane: a Nodal Loop Topological Carbon with \( sp - sp^2 - sp^3 \) Chemical Bonds

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A structurally stable carbon allotrope with plentiful topological properties is predicted by means of first-principles calculations. This novel carbon allotrope possesses the simple space group \( C2/m \), and contains simultaneously \( sp, sp^2 \) and \( sp^3 \) hybridized bonds in one structure, which is thus coined as carboneyane. The calculations on geometrical, vibrational, and electronic properties reveal that carboneyane, with good ductility and a much lower density \( 1.43 \text{ g/cm}^3 \), is a topological metal with two types of Weyl points, nodal loops and nodal network. By comparing its x-ray diffraction pattern with experimental results, we find that carboneyane might already exist in detonation soot. On account of the fluffy structure, carboneyane is shown to have potential applications in areas of storage, absorption and electrode materials.

Carbon is an extremely versatile element in the periodic table, as it can form \( sp, sp^2 \) and \( sp^3 \) hybridized chemical bonds, which thus has a strong ability to bind itself with other elements to generate countless organic compounds with chemical and biological diversity, resulting in the present colorful world. Since 1980s, several new allotropes of elemental carbon, including fullerenes [1], carbon nanotubes [2], and graphene [3], etc., have been synthesized, which inspired numerous attempts to find new structures of carbon in the past decades. According to the Samara Carbon Allotrope Database (SACADA) [4], except the above-mentioned celebrated structures, more than 500 carbon allotropes have been proposed, among which only a few carbon allotropes such as one-dimensional \( sp \)-carbyne [5], two-dimensional \( sp\-sp^2\)-graphdiyne [6], and three-dimensional \( sp^3 \) T-carbon [7, 8], etc. were synthesized in experiments. In addition, there are many carbon allotropes with e.g. \( sp^2 \) [9], \( sp^3 \) [10], \( sp\-sp^3 \) [11, 12], \( sp^2\-sp^3 \) [13, 14] hybridized bonds have been predicted. However, there is no reported carbon allotrope that contains simultaneously all \( sp, sp^2 \) and \( sp^3 \) hybridized chemical bonds in one structure that may display very intriguing physical and chemical properties.

In this paper, we propose a new carbon allotrope that contains three types of hybridized chemical bonds \( sp, sp^2 \) and \( sp^3 \) of carbon atoms in one structure, thus coined as carboneyane, which is energetically and kinetically stable and with a much lower density \( 1.43 \text{ g/cm}^3 \). It has a simple space group \( C2/m \), and is a topological metal that possesses plentiful topological properties, including nodal loops, nodal network and two types of Weyl points. In addition, because of its fluffy structure, we find that carboneyane could be a promising storage material for Li, K and Mg atoms, and a good anode material for lithium-ion and magnesium-ion batteries, revealing that it might have wide applications.

The first-principles calculations were done with the Vienna \textit{ab initio} simulation package (VASP) using the projector augmented wave (PAW) method in the framework of density functional theory (DFT) [15–17]. The electron exchange-correlation functional was described by the generalized gradient approximation (GGA) in the form proposed by Perdew, Burke, and Ernzerhof (PBE) [18]. The structure relaxation considering both atomic positions and lattice vectors was performed by the conjugate gradient (CG) scheme until the maximum force on each atom was less than 0.001 eV/Å, and the total energy was converged to \( 10^{-6} \text{ eV} \) with Gaussian smearing method. The energy cutoff of the plane waves was chosen as 520 eV. The Brillouin zone (BZ) integration was sampled by using a \( 7 \times 13 \times 13 \) G-centered Monkhorst-Pack grid for the calculations of relaxation and electronic structures. The phonon frequencies were calculated using a finite displacement approach as implemented in the PHONOPY code [19], in which a \( 2 \times 2 \times 2 \) supercell containing 128 carbon atoms and a displacement of 0.01 Å from the equilibrium atomic positions are employed. An effective tight-binding Hamiltonian constructed from the maximally localized Wannier functions (MLWF) was used to investigate the surface states [20, 21]. The iterative Green function method [22] was used with the package WannierTools [23].

The geometric structure of carboneyane is shown in Fig. 1. The unit cell contains 16 C atoms, where three unit vectors are \( \vec{a}_1= (a, 0, 0), \vec{a}_2= (0, b, 0), \vec{a}_3= (c \cos \beta, 0, c \sin \beta) \) with \( a=8.80 \text{ Å}, b=5.11 \text{ Å}, c=4.96 \text{ Å} \) and \( \beta=88.28^\circ \). The carbon atoms in carboneyane are classified into three types by bonding nature, where C1, C2, C3 represent \( sp, sp^2 \) and \( sp^3 \) hybridized carbon atoms colored by red, green and blue, respectively, and the ra-
FIG. 1. (Color online) (a) The geometrical structure of carboneyane, and views from (b) [001], (c) [010] and (d) [111] directions. (e) The unit cell of carboneyane, where the carbon atoms are classified into three types C1, C2, C3 by bonding nature, and the red, green and blue colored bonds represent triple, double and single bonds, respectively. (f) The Brillouin zone (BZ) of carboneyane.

TABLE I. The equilibrium density ($\rho$), bond length ($d$), cohesive energy ($E_{coh}$), bulk modulus ($B$), and chemical bonds of cubic and hexagonal diamond, graphite, T-carbon, graphdiyne and carboneyane.

| Structure   | $\rho$ (g/cm$^3$) | $d$ (Å)   | $E_{coh}$ (eV/atom) | $B$(10$^2$ GPa) | bonds     |
|-------------|------------------|-----------|---------------------|----------------|-----------|
| c-diamond   | 3.52             | 1.544     | 7.76                | 4.64           | $sp^3$    |
| h-diamond   | 3.52             | 1.539, 1.561 | 7.73               | 4.30           | $sp^3$    |
| graphite    | 2.22             | 1.422     | 7.89                | 2.94           | $sp^2$    |
| T-carbon    | 1.50             | 1.502, 1.417 | 6.57               | 1.69           | $sp^3$    |
| graphdiyne  | 1.233-1.432      | 7.11      |                     |                | $sp-sp^2$-sp$^3$ |
| carboneyane | 1.43             | 1.218-1.544 | 6.92               | 1.40           | $sp-sp^2$-sp$^3$ |

The equilibrium density ($\rho$), bond length ($d$), cohesive energy ($E_{coh}$), bulk modulus ($B$), and hybridized chemical bonds of cubic and hexagonal diamond [24], graphite, T-carbon [7], graphdiyne [6] and carboneyane are summarized in Table I for comparison. Note that all data presented here were obtained by ourselves using the same method as carboneyane, which can thus be compared reasonably at the same level. Our calculations indicate that the cohesive energy per atom of carboneyane is 6.92 eV, around 0.35 eV/atom higher than T-carbon at the GGA level, suggesting that this structure could be synthesized. Because of its fluffy structure, carboneyane possesses the smallest equilibrium density and bulk modulus among diamond, graphite and T-carbon.

The geometric structure of carboneyane is energetically stable, and the minimum energy per atom is -8.27 eV, which is lower than T-carbon but higher than other carbon allotropes, indicating it is a thermodynamically metastable phase, as shown in Fig. S1 (a) (Supplemental Material). By calculating the enthalpy of carboneyane, as given in Fig. S1 (b), it is obvious that carboneyane possesses an enthalpy lower than T-carbon, indicating it is more stable and can be formed easier than T-carbon. Beyond negative 14.2 GPa, it appears that carboneyane is more stable than diamond in the sense that the relative enthalpy becomes less than zero in this case. To confirm the kinetic stability of carboneyane, its phonon spectra and density of states (DOS) were calculated, as presented in Fig. S2. The obtained phonon eigenvalues can be well explained by considering the bonding nature of the single, double and triple carbon-carbon bonds in this allotrope. No negative frequency phonon is observed in the whole BZ, indicating that carboneyane is kinetically stable. To further examine the thermal stability, we performed ab initio molecular dynamics simulations using a $2 \times 2 \times 2$ supercell containing 128 carbon atoms. After being heated at 300 K and 500 K for 3 ps with a time step of 1 fs, no structural changes occur, revealing that carboneyane is viable for experimental synthesis.

To assess the mechanical properties of carboneyane, its elastic constants were calculated, which gives $C_{11}$, $C_{22}$, $C_{33}$, $C_{44}$, $C_{55}$, $C_{66}$, $C_{12}$, $C_{13}$, $C_{23}$, $C_{15}$, $C_{25}$, $C_{35}$
and C_{46} 236.4, 447.8, 426, 95.2, 82, 20.1, 86.8, 58.4, 7.9, 34.9, 26.2, 82.7 and 22.1 GPa, respectively. These values meet the criteria of mechanical stability for monoclinic phase [29]. In terms of the Voigt-Reuss-Hill approximations [30], we can acquire the bulk B and shear G modulus of carboneyane, say 140 and 74 GPa, respectively. The calculated ratio B/G is 1.89, indicating that carboneyane is ductile, because a high (low) B/G value is associated with ductility (brittleness), and the critical value that separates ductile and brittle materials is about 1.75 according to Pugh’s rule [31]. Young’s modulus E and Poisson’s ratio μ of carboneyane are obtained by $E = 9BG/(3B + G) = 189$ GPa, $μ = (3B − 2G)/(2(3B + G)) = 0.275$. The smaller Poisson’s ratio compared with 0.318 of T-carbon [7] indicates that the bonding is more directional in carboneyane.

To better understand the bonding nature of electrons in carboneyane, the electron charge density, electron density difference (EDD) and electron localization function (ELF) maps are illustrated in Fig. 2. The EDD maps reflect the variation of electron density in terms of chemical bonding, as an EDD is plotted by subtracting the overlapping atomic electron density from the self-consistent electron density of carboneyane. The ELF maps give a clear and quantitative description on the basic chemical bonds [high ELF values (0.5 < ELF < 1) indicate the formation of covalent bonds] [32–34]. It is instructive to note from Figs. 2 (a) and (b) that electrons in carboneyane are localized on (001) plane along the armchair (y-axis) direction including $sp^2$ carbon atoms and on (010) plane along the zigzag (z-axis) direction containing $sp$ and $sp^3$ carbon atoms. From the EDD maps shown in Figs. 2 (c) and (d), we can see that there is a larger gain of electron density between triple bonded carbons. Meanwhile, from the ELF maps shown in Figs. 2 (e) and (f),
we find that there is an enhanced localization between triple bonded carbons clearly, which is larger than the localization between the single and double bonded carbons. These results show that the bonding strength of the hybridized bonds $sp$, $sp^2$, and $sp^3$ in carboneyane are different, where the $sp$ bond is the strongest while both $sp^2$ and $sp^3$ bonds are comparable.

To provide more information for possible experimental identification, we also simulated the x-ray diffraction (XRD) spectra of carboneyane with wavelength 1.54 Å. The results are presented in Fig. 3 (a). The XRD peaks appear at the angles $2\theta = 17.9^\circ$ of (001), $20.1^\circ$ of (110), $26.7^\circ$ of (201), $27.2^\circ$ of (11T), $27.5^\circ$ of (20T), $35.1^\circ$ of (020), $36.2^\circ$ of (002), $39.4^\circ$ of (311) and $40.8^\circ$ of (220) planes. It is interesting that in detonation soot samples Alaska A, B and C [25] with different carbon concentrations, the most remarkable feature of the experimental XRD spectra is the peak around $26.7^\circ$, which well matches one of calculated XRD peaks of carboneyane. Besides, the experimental peaks around $35.1^\circ$ and $39.4^\circ$ of the detonation soot also meet with the calculated data of carboneyane. This observation suggests that carboneyane might be a possible candidate of the carbon phase observed in the detonation soot.

The simulated Raman and infrared (IR) vibrational modes with corresponding frequencies are presented in Figs. 3 (b) and (c), respectively. The Raman spectra exhibit a well-marked peak at 1760 cm$^{-1}$. The IR spectra show a number of peaks within the wavelength of 5 μm and 30 μm. These attainable features may be useful for experimentally identifying carboneyane in future.

The band structures and partial DOS (PDOS) calculated within the GGA are shown in Fig. 4. In the band structure, there appear linear band crossing points along Γ-B, Γ-Y, Γ-Z, Z-D and B-D paths very close to the Fermi level. Through a careful inspection on the crossing points in the BZ, we observe that the two type-I Weyl points along Γ-B and Γ-Y belong to a nodal loop centered around Γ point in the $k_x = 0$ plane, the two type-I Weyl points along Γ-Y and Γ-Z belong to a nodal loop centered around Γ point in the $k_x = 0$ plane, and a nodal network is comprised of the type-I and type-II Weyl points along Γ-B, Γ-Z, Z-D and B-D in the $k_y = 0$ plane, as shown in Figs. 5 (a)-(c), where we plot the local gap between the two crossing bands in the $k_x = 0$, $k_y = 0$ and $k_z = 0$ planes, respectively. One may see that there are two paths along the D loops in these planes. The nodal loops including the nodal network are protected by the coexistence of time-reversal and inversion symmetries. Besides the nodal loops, there exist two pairs of type-II Weyl points at energy -0.05 eV below the Fermi level. The two pairs of Weyl fermions are verified by the existence of Fermi arcs as shown in Fig. 5 (d).

From the electronic band structure, one may observe that there are also double degeneracy appearing on the high-symmetry paths, and such a degeneracy is ensured by the symmetry of the system. Let us first consider the degeneracy along $D$-$E$ and $A$-$B$ paths with $k_x = \pi$. Any $k$ point on these paths is invariant under the combined operation $T \mathcal{M}_y$ [$T$ is the time reversal operator and $\mathcal{M}_y$: $(x, y, z) \rightarrow (x+1/2, -y+1/2, z)$ is a glide mirror]. We note $(T \mathcal{M}_y)^2 = T_{100} = e^{-ikx} = -1$, where we have used $T^2 = 1$ for the spinless case. This anti-unitary operator thus generates a Kramers-like double degeneracy on $D$-$E$ and $A$-$B$ paths. The whole plane with $k_y = \pi$ form invariant subspaces for the combined operator $T \mathcal{S}_{2y}$ [$\mathcal{S}_{2y}$: $(y, x, z) \rightarrow -(x+1/2, y+1/2, -z)$ denotes screw symmetry]. For the combined operator, we have $(T \mathcal{S}_{2y})^2 = T_{010} = e^{-iky} = -1$, thus it can protect a Kramers-like double degeneracy on the $k_y = \pi$ plane.

The spin-orbit coupling (SOC), which opens up a small gap about 0.1 meV at the band crossing points according to our calculations, is negligibly weak, and thus does not alter the metallic nature of carboneyane.

From the PDOS, we can observe that the states around the Fermi level come mainly from the $p_z$ orbitals, which determine the metallic nature of carboneyane. Via a careful analysis on PDOS near the Fermi level (-0.3-0.3 eV) [Fig. S3 (a)], we uncover that the $p_z$ orbitals near the Fermi level are from π-electron of $sp^2$ hybridized carbon atoms on the (001) plane, giving rise to the conductive property of caboneyane. By computing the conductivity of carboneyane with the package BoltzTrap [35], we find that the conductivity $\sigma_{yy}$ is about 40 times of $\sigma_{xx}/\pi$ and about 400 times of $\sigma_{zz}/\pi$ with the relaxation time of electrons, indicating a strong anisotropic conductivity [Fig. S3 (b)].

Carboneyane possesses a unique fluffy structure with...
large interspace between carbon atoms, making it easy to hold atoms for absorption and migration. We investigated the absorption and diffusion of alkali (Li, Na, K) and alkaline earth (Mg) atoms in carboneyane. The results are collected in Table S1. From Table S1 one may find that the maximal specific capacity was estimated to be 588 mAhg\(^{-1}\) for Li, K, Mg atoms, which is larger than that in graphite (372 mAhg\(^{-1}\)). In addition, the doped Li structure exhibits potential as an ideal anode electrode, which has a remarkable ion migrating barrier of only 0.094 eV much lower than 0.327 eV in graphite. Carboneyane also exhibits a very low voltage, high storage capacity and small volume deformation for Mg ion. Thus, carboneyane could be a good storage and absorption material for Li, K and Mg atoms, and a promising anode material for lithium-ion and magnesium-ion batteries.

In summary, by means of first-principle calculations we proposed for the first time a novel carbon allotrope dubbed as carboneyane which contains simultaneously sp, sp\(^2\) and sp\(^3\) hybridized chemical bonds in one structure. This carbon allotrope, with a ductile and directional structure, is the lightest among the known three-dimensional carbon allotropes. The calculations on electronic properties of carboneyane show that it is a topological metal with nodal loops, nodal network and two types of Weyl fermions connecting valence and conduction bands near the Fermi level. The XRD spectra indicate that carboneyane may already exist in the detonation soot. Upon being obtained, the intriguing carboneyane may be a good storage and absorption material for Li, K and Mg atoms as well as a promising anode material for lithium-ion and magnesium-ion batteries.

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