Electronic and structural properties of 3D Hopf-linked carbon allotrope: Hopfene

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Electronic and structural properties of a 3D carbon allotrope made of Hopf-linked graphenes, which we call a Hopfene - a type of topological crystal, are examined by semi-empirical molecular-orbital and density-functional-theoretical methods, where band-structure analyses reveal very different properties from those of 2D graphenes. Furthermore, the analyses give an interesting finding that, depending on graphene-sheet spacings, Hopfenes exhibit different band features between primary-type Hopfene with a finite minimum sheet spacing and secondary type with its double-sized spacing. The primary type shows semi-metallic nature and the secondary type exhibits semi-metallic or semiconducting nature at different bands and also has flat bands; these conducting features can be utilised by Fermi-level control. A device application of Hopfenes is also provided.

INTRODUCTION

The discovery of carbon allotropes [1–3] unveiled their unusual fundamental physical properties via electrical and spectroscopic analyses [4–6], albeit using only one type of material - carbon. Their scientific applications harnessing morphological features together with electronic states realised there have been powerfully made in condensed-matter physics; for example, superconductivity in alkali-metal-doped fullerences [7], Tomonaga-Luttinger liquid in carbon nanotubes [8], and quantum Hall effect (QHE) [9,10] and Kosterlitz-Thouless (KT) transition [11] in graphenes. Of these, the findings of fullerenes and graphenes, which imply those outstanding scientific applications, received Nobel chemistry and physics prizes in 1996 and 2010, respectively, and also their useful functionalities have since then spread all over material science and nano-electronics.

On the other hand, 'topology' is now one of the important keywords to deeply understand new kinds of condensed-matter physics, such as QHE in terms of the Chern number, KT transition caused by vortex pairs (topological-defect pairs), and topological insulators and superconductors. Inspired by those new standpoints, we have proposed a variety of topological carbon structures in the form of a molecule, a chain, a chainmail, and a crystal [12]. Among them, such topological crystals made of graphenes as in Figs. 1(a)(b) are of particular interest (where their stability is kept by insertion of finite-sized vertical graphene layers into infinitely-large horizontal graphene layers [13]; to set stress free, the crystal size here is assumed to be much greater than atomic-structure periods in the crystal).

Despite using graphenes, those topological crystals may exhibit qualitatively different electrical properties from the graphenes with semiconducting nature [14] because of different topologies; however, their precise characteristics are not yet clear, not even clear whether the proposed crystals are metallic, semi-metallic, or insulating. The present paper clarifies this point by band-structure analyses using a density-functional-theoretical (DFT) method [15–17], where semi-empirical molecular-orbital (MO) analyses [18] are also used for structural analyses.

Structurally-optimized crystals, as shown in Figs. 1(a)(b) via the semi-empirical MO method, have Hopf-links at their intersections. We thus call these crystals Hopfenes after topologist Heinz Hopf who studied those links in detail. The Hopfenes in Figs. 1(a)(b) have atomic symmetry $P4_{2}bc$ and $P4_{2}$, respectively.

A Hopf-link, as illustrated in Fig. 2(a), is the building block of Hopfenes. Calculated energy of forming a single Hopf-link is high ($\sim 600$ kcal/mol), so that the single link will require a high compressive pressure for its stable existence in nature (thus it may be found in coke stones at a place deep under the ground). Embedding Hopf-links...
in the Hopfene helps the link stability. In Fig. 2(b), or a schematic diagram of a link when including more than six carbon atoms in its ring, the formation energy is lowered, and the link is realised by chemical synthesis at 1 atm [20]. If polymers are used in place of carbons, it is known that the Hopfene can be achieved [21, 22] (but with slightly different atomic symmetry I4/mcm). The nature of such topological crystals as Hopfenes is interesting, but their electrical conduction is unknown; the electrical conduction is a very important property in crystals. The present paper thus focuses on the study of electrical conduction via band-structure analyses, which will show very different features from those of 2D graphenes; furthermore, a difference in graphene-layer spacing will provide different properties in electrical conduction.

The paper is organized as follows: § provides the details of carbon Hopfene structures; § gives analysed results of wavefunctions and band structures of the Hopfenes and also discusses the obtained results; and § provides a summary.

CARBON HOPFENE STRUCTURES

Hopfenes have some different types, as seen in Figs. 1(a)(b), with respect to graphene-sheet spacings and sheet phase-shifts. Figure 1(a) shows that the slot-1 sheet inserted horizontally (i.e., parallelly to the x-z plane) is set to the exact middle between slot-0 and slot-2 sheets so that horizontal σ-bond ladders between zigzag edges intersect vertical σ-bond ladders between other zigzag edges; this causes a half-lattice-constant shift (or a phase π-shift) at the slot-1 sheet as long as the slot-1 sheet is set between slot-0 and slot-2 sheets (i.e., with no empty slots), where slot-0 and slot-2 sheets have no phase shift for each other. This configuration precludes the insertion of other sheets in parallel to the x-y plane. We call this type of Hopfene a (1,1)-Hopfene. On the other hand, Fig. 1(b) depicts a Hopfene where the slot-1 sheet is removed (for other parts in the horizontal direction, similar removal is made); the same sheet removal in the vertical direction is also made. We call this type of Hopfene a (2,2)-Hopfene, which has no phase-shifted sheets for parallelly-aligned sheets.

Both (1,1)- and (2,2)-Hopfenes have a tetragonal unit cell with lattice constants of a and b (= a) in the x and y directions and c (≠ a = b) in the z direction. It seems that the period in Fig. 1(b) in the x and y directions is double as large as that in Fig. 1(a). But since the graphene sheet at slot 1 in Fig. 1(a) is π-shifted in the z direction, both periods in the x and y directions in Figs. 1(a)(b) are the same. In Fig. 1(a), although there remains the phase π-shift at the slot-1 sheet in the z direction, the Hopfene periods at the slot-1 sheet in the z direction both in Figs. 1(a)(b) are actually the same; the difference is the cross-sectional atomic configuration.

WAVEFUNCTION AND BAND-STRUCTURE ANALYSES

We then analyse electron wavefunctions and band structures of the Hopfenes by the DFT method. As is well-known, the band structure of 3D molecular crystals made up of such molecules as 2D saturated hydrocarbons with σ-bonds is not so much different in bandgap from that of isolated molecules with a HOMO-LUMO energy gap. But, forming a honeycomb structure (without hydrogens), i.e., a graphene, changes the situation, producing an electronic band with a zero gap, where extended π-orbital wavefunctions are allowed, as seen in Fig. 3(a) on the upper and lower graphene surfaces; this also recovers electrical conduction (if the Fermi level is set higher or lower than the Dirac point by donor- or acceptor-doping or by gate-field application when using a field-effect-transistor structure).

In the (1,1)-Hopfene, extended π-orbitals, obtained by numerically solving the Kohn-Sham equation, go in the vertical direction as well as in the horizontal direction, as displayed in yellow in Figs. 3(b)-(d); these figures include other Kohn-Sham-wavefunction contributions painted in blue and light blue. These blue and light blue ones are actually the same; the difference is the cross-sectional atomic configuration.
FIG. 3. (a) $\pi$-orbital wavefunctions formed on the upper and lower graphene surfaces, where the vertical axis is in a normalized unit. (b) Electron probability distribution patterns including horizontally and vertically extended $\pi$-orbitals, indicated in yellow (normalized unit) for the (1,1)-Hopfene, occupying the intermediate region of the Hopf-link at the cross-section containing carbon No. 1, 4, 8, 9. The carbon atoms have localised electrons around them, indicated in blue. Regions with very small wavefunction amplitudes (or almost no electron regions) are indicated in orange. (c) Intermediate cross-section between (b) and (d), where the extended $\pi$-orbitals almost fully occupy the region, except the ‘orange’ holes; localised electrons around the $\sigma$-bonds are indicated in light blue. (d) Similar to (b) but at the cross-section containing carbon No. 2, 3, 7, 10. For carbon No. 7, 8, 9, 10, refer to Fig. 2(a).

FIG. 4. Band structures of (a) (1,1)-Hopfene and (b) (2,2)-Hopfene, where the lattice constants are $a = b = 5.1$ Å and $c = 2.6$ Å. Here, the electron energy $E$ in the vertical axis is measured from the Fermi level $E_F$.

We also observed several flat bands in Fig. 4(b). So far the mechanism of this flat-band appearance has not yet been well understood; but we have simultaneously observed a great decrease in the number of dispersion branches with branch rearrangement (with increasing degeneracy). We thus infer that this flat-band appearance is intimately related to this increased degeneracy, which results from the higher crystal symmetry of the (2,2)-Hopfene with no phase-shifted sheets than that of the (1,1)-Hopfene with a large number of phase-shifted sheets. The presence of flat bands is interesting, and actually very useful in solid-state physics; for example, this makes it possible to study the ground-state property of a many-body carrier system in a nonperturbative manner, and the Hopfene can be a type of itinerant carrier system that provides such a possibility.

As for details of the band structure of the (1,1)-Hopfene in Fig. 4(a), we can see that the band is clearly semimetallic because it has partially filled conduction and valence bands (valleys), which are caused by the graphene-intertwined structure and thus clearly differ from the band of 2D graphenes. In Fig. 4(b) for the (2,2)-Hopfene, we can see semi-metallic or semiconducting parts at different bands and also see several flat bands; those bands can be utilised by Fermi-level shifting with, e.g., doping. (But too much doping should be avoided to prevent a large band-structure deformation.) Here, since the flat bands have high density of states (DOS) with carriers having very large effective mass, if the Fermi level is set to a flat band, the electron-interaction term is dominant in the competition between electron kinetic-energy and interaction terms in an $e-e$-interaction Hamiltonian, such as the Hubbard Hamiltonian, which could cause ferromagnetism [24–27]. Research on Hopfenes is very interesting, and we expect that more interesting properties will come from it, including BCS-BES crossover and superconductivity-insulator transition [28].

On the application side of Hopfenes, since chemical sensors with a graphene, for example, currently have a low adsorption rate of gas molecules on the graphene, if we replace the graphene with a Hopfene with some electrical conduction and use Hopfene’s holes (nanopores) to effectively capture the gas molecules, the sensor will obtain a high adsorption rate, thus enhancing its sensitivity, where sensing is made via a change in the electrical...
conduction when molecule adsorption occurs.

CONCLUSIONS

We have proposed Hopf-linked carbon allotropes, named Hopfenes, with the help of structural analyses via a semi-empirical MO method (where Hopfenes are assumed to be much larger in size than their lattice periods and supported in large graphenes). We then have analysed the electron wavefunctions of a Hopfene by DFT analyses, which show that its Hopf-links in extended π-orbitals are standing well (n.b., polymer Hopfenes in the same situation are known to exist experimentally). The DFT band-structure analyses have exhibited that unlike 2D graphenes with semiconducting nature with a zero gap, (1,1)-Hopfenes are semi-metallic and that (2,2)-Hopfenes are semi-metallic or semiconducting at different bands and have several flat bands; these can be utilised by Fermi-level control. The proposed carbon Hopfenes have not yet been realised, but if they are produced or found, they can be used for interesting electrical-conduction and magnetism research and also for sensor applications.

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DISCLOSURE STATEMENT

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