

First-Principles Computational Studies of the Electronic and Optical Properties of M-C16 Carbon

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Abstract: Based on the first-principles calculation method of density functional theory, we designed a new all-sp² hybrid M-C16 carbon with a zigzag carbon chain. The results show that M-C16 carbon has good stability and symmetric nodes appear in the Brillouin zone of this structure. Moreover, we further studied the optical properties of M-C16 carbon, which showed that it has a strong absorption in the ultraviolet range and can be used in solar cells and optoelectronic devices. This study not only provides new ideas for the construction of novel 3 D topological carbon allotropes, but also promotes the development of novel carbon allotropes with novel electron and transport properties.

Keywords: First-Principles Calculation; Optical Properties; Graphene

1. Introduction

The discovery of fullerenes opened a new "era of the carbon allotypes"^[1-4], for which many carbon structures have been proposed. These carbon allotropes are functionally diverse, which mainly depends on the different coordination number it forms with itself, that is, the different way of hybridization. In the periodic table, carbon is the only known element with one-, two-, and three-dimensional stable allotropes. From the bond mode, carbon atoms can form coordination numbers from 2 to 4, corresponding to the hybrid mode from sp to sp³ hybrid^[5]; from the bond shape, carbon can form single, double and triple bonds. Due to the "quadrivalent" principle of carbon, it can also form various compounds with other atoms; from the perspective of conductive performance, carbon can exist as a conductor in^[6] in graphite and graphene formed by sp² hybrid, and can become an insulator^[7-8] with broadband gap in diamond formed by sp³ hybrid. Therefore, the search for new carbon allotropes and find their excellent performance has been an active research field.

The appearance of topological materials also brings people a different world, especially in topological semimetals, a series of novel physical properties, such as "drum surface" surface states, Fermi arc and chiral anomalies and so on^[9-10]. These peculiar physical properties also give topological semimetal materials some potential applications in chemical catalysis, quantum computing, and spintronics. For now, most of the studies on topological semimetals are still on heavy metal elements, and the light elements of SOC provide a platform for the study of topological materials. Taking carbon atoms as an example, the rich electronic and topological properties of the new carbon allotrope not only attract theoretical exploration, but also attract extensive experimental attention for its interesting physical phenomena and potential applications^[11-15]. Among them, some carbon structures have been synthesized, such as graphene, T-carbon, CHC and other^[16-18]. The ability to predict novel carbon structures and their chemical and physical properties using theoretical methods has also improved in recent years.

The structure contains 16 atoms in the protocell and belongs to a monoclinic crystal system. Using a density functional theory approach, we calculate the stability, electronic and optical properties of M-C16 carbon. The tational results including phonon spectrum, elastic constants and first molecular dynamics show a good stability of M-C16 carbon. The electronic band calculation show that this structure appears symmetric nodes in the BZ. In addition, we calculate the optical properties of M-C16 carbon, which shows that it has a strong absorption in the UV region and can be used in solar cells and optoelectronic devices.

2. Calculation method

The first-principles calculation in this paper is based on the density functional theory ^[19], using the Perdew-Burke-Ernzerhof (PBE) function ^[20] of the exchange correlation potential of the generalized gradient approximation (GGA). All the calculations were performed in the Vienna Ab initio Simulation software package (VASP). The truncation energy of plane waves was set to 600 eV with an energy convergence accuracy of 10⁻⁵ eV. The atomic positions were fully optimized until the residual force on each atom was less than 10⁻⁵ eV / atom. The first Brillouin area integration was geometrically optimized using a k-point grid of 15917. To calculate the stability of the structure, 222 supercells were simulated with ^[21] by first molecular dynamics (AIMD) using a time step of 10ps.

3. Calculation results and discussion

3.1 Structure and stability

Structurally, graphene is the "parent" of many carbon allotropes, and many carbon structures also inherit the excellent properties of graphene. Therefore, graphene is often seen as the foundation for designing new carbon allotropes. It is well known that graphene is a two-dimensional carbon allotrope composed of sp² hybrid carbon atoms. The valence band and conduction band near the Fermi surface intersect the Dirac point, thus showing Dirac semimetal properties. When graphene is cut, it can be seen to be made of zigzag / armchair-shaped carbon chains. Inspired by the above, we constructed a 3 D carbon allotrope by connecting a zigzag carbon chain, and we believed that this structure contains topological properties. As shown in the side view of Figure 1 (a), the structure is composed of a twisted zigzag carbon chain connection. The 211 supercell of the Figure 1 (b) structure can be seen as a connection of certain atoms at the edge of a twisted zigzag carbon chain. Because this structure contains 16 atoms and belongs to a monoclinic crystal system, it is named M-C16 carbon. The space group of M-C16 carbon is P2 / M (No.10), and its protocell consists of 12 carbon atoms, as shown in Figure 4.1. Its optimized lattice constants are a=4.15Å, b=7.36Å and c=3.32Å, and the angle between a and c is $\beta = 69.2^\circ$. Its bond length is between 1.40 Å and 1.48 Å, which is similar to that of graphene (1.42Å). The structure is composed entirely of sp² hybrid carbon atoms and shows good stability.

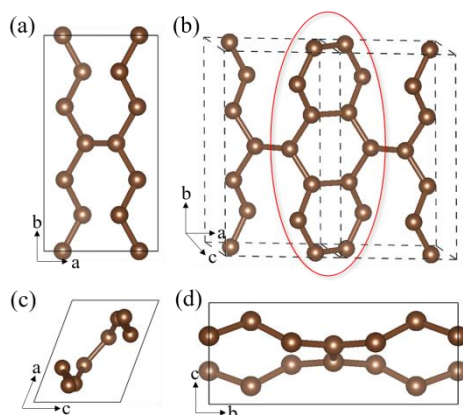


Fig.1 (a) Side view of M-C16 carbon primary cell; (b) side view of $2 \times 1 \times 1$ supercell of M-C16 carbon; (c) top view of

M-C16 carbon primary cell; (d) M-C16 Another side view of carbon primitive cell

As calculated by first-principles methods, the binding energy of M-C16 carbon is $E_{\text{coh}} = 7.54 \text{ eV/atom}$, which is 0.36 eV/atom higher than graphite and diamond (7.77 eV/atom) (7.90 eV/atom), but 0.99 eV/atom lower than that of T-carbon (6.55 eV/atom). Since T-carbon has been successfully synthesized experimentally, M-C16 carbon is expected to be successfully prepared experimentally in the future. To further verify the dynamical stability of M-C16 carbon, we compute its phonon dispersion spectrum. As shown in Figure 2 (a), the phonon spectrum of M-C16 carbon does not have an imaginary frequency in the entire Brillouin zone, indicating that it is a metastable structure. In addition, we also calculated the first molecular dynamics simulation of M-C16 carbon at 300 K temperature in regular system (NVT), such as the total energy of the structure basically stable within 10 ps , and the crystal structure shown in Figure 2 (b) in the constant temperature at 300 K is not destroyed, which further verified the thermodynamic stability of the structure.

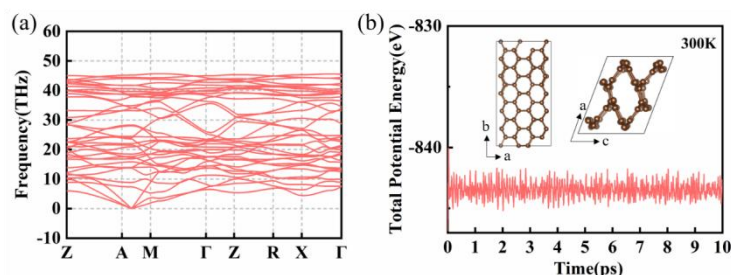


Fig.2 (a) Phonon spectrum of M-C16 carbon; (b) AIMD simulation image of M-C16 carbon at 300 K

3.2 Electronic properties

The electronic properties of M-C16 carbon are analyzed. Figure 3 (A) shows the electronic band structure of the structure (left part) and the corresponding projected density of states (PDOS) (shown in the right part). From the band map, we can see that the conduction band and the valence band of M-C16 carbon form an intersection near the Fermi level, located on the abscissa high symmetry path D-E in the band map. As can be seen from the PDOS in the right part of Figure 4.3 (a), the band intersection near the Fermi surface is mainly contributed by the p_x and p_z orbitals of the carbon atoms. To gain a clearer understanding of the linear dispersion relation of the bands, we further calculate the M-C16 carbon electronic properties. The results are shown in the topological phase in Figure 3 (b), where there are four independent nodes in the first BZ of M-C16 carbon. Subsequently, we took two points P1 and P2 near the intersection of the energy band, and calculated the wave function of the two points (as shown in Figure 4). From the top view and side view of the wave function, we can see that the source of electron distribution at P1 is relatively uniform, and almost all atoms in the structure have a certain contribution. However, at point P2, the electron distribution is mainly contributed by the zigzag carbon chain atoms at the non-junction.

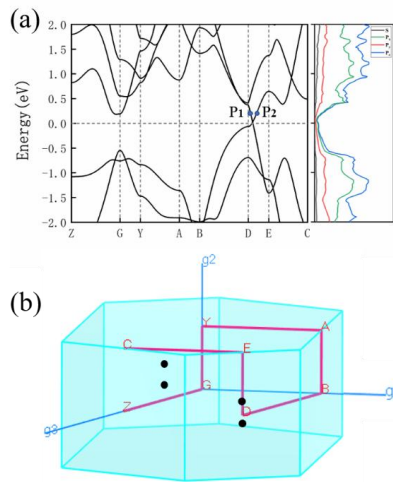


Fig.3 (a) Band structure and PDOS of M-C16 carbon; (b) the BZ and topological phase of M-C16 carbon

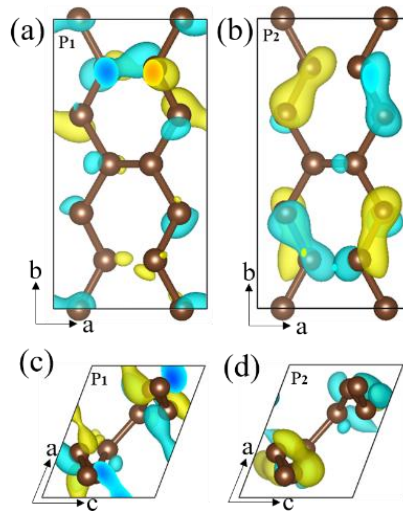


Fig.4 (a) (c) are the side view and top view of the wave function at point P₁ in the band structure in Figure 4.3; (b) (d) are the side view and top view of the wave function at point P₂, respectively

3.3 Optical properties

To gain insight into the optical properties of M-C16 carbon, we calculate the imaginary part of the dielectric function and the absorption coefficient of the structure. The imaginary part of the dielectric function in Figure 5 (a) shows that M-C16 carbon is anisotropic. As can be seen from the absorption coefficient spectrum of Figure 4.5 (b), the absorption coefficient of the three directions of M-C16 carbon is almost the same in the ultraviolet region 0-1.2eV, while it is obvious difference in the visible region and the infrared region. wherein light absorption in the x direction in the visible region > light absorption in the y direction > light absorption in the z direction. x is more complicated in the infrared region. However, the absorption coefficient of the system reaches 10⁵ exponential level, which also shows that M-C16 carbon is promising in broad spectrum devices.

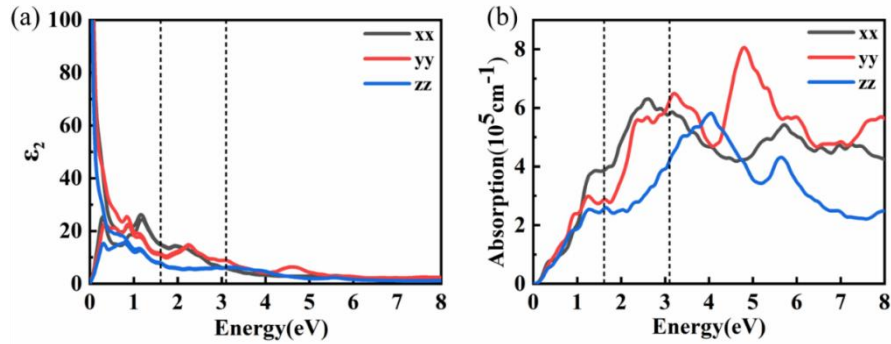


Fig.5 (a) The imaginary part of the dielectric function of M-C16 carbon. (b) Absorption coefficient spectrum of M-C16 carbon

4. Conclusion

In this paper, we propose a new carbon allotrope M-C16 carbon with a three-dimensional full sp^2 hybrid constructed from a zigzag carbon chain, which can be regarded as a twisted graphene structure. Based on the first-principle method, we calculated the stability of M-C16 carbon from three aspects of dynamic, thermodynamic and mechanical stability, and the results show that the structure has good stability. An analysis of the electronic properties of M-C16 carbon then shows that the structure has symmetric nodes in the BZ. Moreover, the optical properties of the structure indicate that it has strong absorption in the UV region and can be used in device studies. The present study not only provides a prospect for new electronic structures of carbon allotropes, but also facilitates future exploration of novel carbon allotropes with novel electronic and transport properties.

References

- [1] Kroto HW, Heath JR, O'Brien SC, et al. C60: Buckminsterfullerene[J]. *Nature*, 1985, 318(6042): 162-163.
- [2] Tiwari SK, Kumar V, Huczko A, et al. Magical Allotropes of Carbon: Prospects and Applications[J]. *Critical Reviews in Solid State and Materials Sciences*, 2016, 41(4): 257-317.
- [3] He C, Sun L, Zhang C, et al. New superhard carbon phases between graphite and diamond[J]. *Solid State Communications*, 2012, 152(16): 1560-1563.
- [4] Heimann RB, Evsvukov SE, Koga Y. Carbon allotropes: a suggested classification scheme based on valence orbital hybridization[J]. *Carbon*, 1997, 35(10): 1654-1658.
- [5] Wang Y, Yang P, Zheng L, et al. Carbon nanomaterials with sp^2 or/and sp hybridization in energy conversion and storage applications: A review[J]. *Energy Storage Materials*, 2020, 26: 349-370.
- [6] Novoselov KS, Geim AK, Morozov SV, et al. Electric Field Effect in Atomically Thin Carbon Films[J]. *Science*, 2004, 306(5696): 666-669.
- [7] Bragg WH, Bragg WL. The structure of the diamond[J]. *Proceedings of the Royal Society of London. Series A, Containing Papers of a Mathematical and Physical Character*, 1913, 89(610): 277-291.
- [8] May PW. Diamond thin films: a 21st-century material[J]. *Philosophical Transactions of the Royal Society of London. Series A: Mathematical, Physical and Engineering Sciences*, 2000, 358(1766): 473-495.
- [9] Yang HF, Yang LX, Liu ZK, et al. Topological Lifshitz transitions and Fermi arc manipulation in Weyl semimetal NbAs[J]. *Nature Communications*, 2019, 10(1): 3478.
- [10] Xu SY, Liu C, Kushwaha SK, et al. Observation of Fermi arc surface states in a topological metal[J]. *Science*, 2015, 347(6219): 294-298.
- [11] Castro Neto AH. The carbon new age[J]. *Materials Today*, 2010, 13(3): 12-17.
- [12] Soluyanov AA, Gresch D, Wang Z, et al. Type-II Weyl semimetals[J]. *Nature*, 2015, 527(7579): 495-498.

- [13] Cheng Y, Du J, Melnik R, et al. Novel three dimensional topological nodal line semimetallic carbon[J]. Carbon, 2016, 98: 468-473.
- [14] Zhao Z, Hang Y, Zhang Z, et al. Topological hybrid nodal-loop semimetal in a carbon allotrope constructed by interconnected Riemann surfaces[J]. Physical Review B, 2019, 100(11): 115420.
- [15] Xie Y, Gong C, Zhou J, et al. Design triple points, nexus points, and related topological phases by stacking monolayers[J]. Applied Physics Letters, 2019, 115(7): 073105.
- [16] Sheng XL, Yan QB, Ye F, et al. T-Carbon: A Novel Carbon Allotrope[J]. Physical Review Letters, 2011, 106(15): 155703.
- [17] Gao Y, Chen Y, Zhong C, et al. Electron and phonon properties and gas storage in carbon honeycombs[J]. Nanoscale, 2016, 8(26): 12863-12868.
- [18] Krainyukova NV, Zubarev EN. Carbon Honeycomb High Capacity Storage for Gaseous and Liquid Species[J]. Physical Review Letters, 2016, 116(5): 055501.
- [19] Perdew JP, Chevary JA, Vosko SH, et al. Atoms, molecules, solids, and surfaces: Applications of the generalized gradient approximation for exchange and correlation[J]. Physical Review B, 1992, 46(11): 6671-6687.
- [20] Grimme S. Semiempirical GGA-type density functional constructed with a long-range dispersion correction[J]. Journal of computational chemistry, 2006, 27(15): 1787-1799.
- [21] Nosé S. A unified formulation of the constant temperature molecular dynamics methods[J]. The Journal of Chemical Physics, 1984, 81(1): 511-519.