Density functional theory study on electrical properties of graphyne propane under tension and compression deformation

Lin Wei, Guili Liu and Guoying Zhang

1 College of architecture and civil engineering, Shenyang University of Technology, Shenyang, Liaoning 110870, People’s Republic of China
2 College of physics, Shenyang Normal University, Shenyang 110034, People’s Republic of China

E-mail: lgl63@sina.cn

Keywords: graphyne, tensile and compression deformation, electronic structure

Abstract

Based on the first-principles of density functional theory, this paper systematically studied the effect of tensile and compression deformation on the electrical properties of graphyne. The study show that the graphyne has an direct and adjustable band gap under deformation. Under uniaxial deformation, the band gap tend to be in the decline with the increase of the deformation, but under biaxial deformation, the band gap is positively correlated with the deformation, which increases with the rising of the tension deformation, and decreases with the increase of the compression deformation. The band gap value calculated by the HSE06 method is larger than what is obtained by the GGA method, but the shape characteristics of the band structure obtained by the two are basically the same, as well as the same trend between band gap and strain. With the tensile and compressive deformations increase, the charge transfer between C atoms in the graphyne is intensified. Compressive deformation makes the graphyne system more stable, while tensile deformation reduces the stability of graphyne. Compared with uniaxial, biaxial deformation has a more severe effect on the stability and band gap of the graphyne system, but less on charge transfer.

1. Introduction

Carbon is the basis for all known organism on Earth, and its elements have numerous allotropes. In addition to the common three-dimensional diamond and graphite, there exist zero-dimensional fullerene [1], one-dimensional carbon nanotubes [2], two-dimensional graphene [3] and so on. Due to the macroscopic differences, the rich allotropy is caused by the different proportions of the orbital hybridization of sp, sp² and sp³ in the composition of carbon materials. Various allotropes form different carbon structures, each of them has unique properties of mechanics, thermals, and magnetism, and the graphyne is one of them. As early as in 1987, the famous theorist Baughman [4] calculated that the graphyne structure could exist in a stabl state. In 2010, it was first proposed by the Li Yuliang and his research group of the Institute of Chemistry of the Chinese Academy of Sciences. Large-area graphdiyne films were successfully synthesized by chemical in situ reaction on copper surfaces [5, 6]. The results of this study confirmed that the graphyne formed by the sp and sp³ hybridization state could be prepared by artificial synthesis, which opened up the road for experimental testing of synthesis [7].

Subsequently, experimental reports on the synthesis of graphyne and graphyne-4 in the experiment, which fully demonstrated the excellent editability and diverse geometry of graphyne [5, 8–10]. At the same time, the research about the application of charge mobility of graphyne [11, 12], mechanical properties [13, 14], nanobelt characteristics [15–17], and electrodes in lithium batteries [18, 19], hydrogen storage and lithium storage [20–26], and gas separation [27] are also about emerge. Graphyne has the natural advantage of being able to perform a large number of preparations at low temperatures and achieve the control of the planar pore size, making up for some of the natural defects of conventional carbon materials. In the design and application of nanodevices, the controlling force of the band gap of materials is of great importance. Compared with the zero band gap of graphene, graphyne with natural direct band gap seems to be more suitable for electronic
applications. It has the ability to get rid of the limitations of zero band gap materials in applications, such as the switching effects of gate bias control for some field effect transistors and conventional semiconductors. Because of its synthesis conditions, its basic structural unit can be precisely designed to realize the regulation of the electronic structure. The actual graphene layer is not a complete plane and there are undulations on the surface. It is in this way that graphene is used to adjust the bond length to maintain its stability. Even if the self-deformation of the graphene is neglected, the application of stress at the edges also causes the graphene sheets to be distorted. Many studies have shown that deformation can change the band gap of materials [28–31]. In fact, the deformed graphene is closer to the actual material than the theoretical planar graphene, and the deformation can lead to different electronic structures of graphene. Since the deformation does not change the chemical composition of the graphene, the effect of the deformation influence on the properties of the graphene has a more unique practical significance. Based on the first-principles method, Kang et al [32] studied the elastic, electronic and optical properties of graphene. The band structure of graphene was calculated using both generalized gradient approximation and hybrid functional, and the latter predicts that the band gap is twice the electronic structure. The actual graphene layer is not a complete plane and there are undulations on the surface.

2. Physical model and calculation method

In this study, density functional theory calculation and analysis are performed on graphene. The calculation is performed by the CASTEP module in the Materials Studio package [33]. The exchange-associated functional uses the generalized gradient approximation of Perdaw–Burke–Ernzerhof (GGA-PBE) [34]. Since GGA underestimates the band gap, the hybrid function Heyd Scuseria Ernzerhof (HSE06) is also used for band structure calculations. The effect of spin polarization is not taken into consideration in the calculation. The truncation energy of the wave function is 350 eV. The integration of the Brillouin zone uses the Monkhorst-Pack special K-point sampling method. In each model structure optimization, the K-point grid is taken as $6 \times 6 \times 1$. The calculation takes the Z direction perpendicular to the plane of the graphene, The X and Y planes are parallel to the plane of the graphene. In order to study the single-layer structure of graphene, and to eliminate the interference of periodic mirror atoms, a vacuum layer with a thickness of 15 Å is placed in the direction of the unit cell Z of the vertical graphene plane. In the calculation, the original cell shape of the established model and the atomic position in the original cell are fully relaxed, and the total energy of each atom is not less than $2.0 \times 10^{-6} \text{eV \ atom}^{-1}$. All the atomic forces are less than 0.05 eV nm$^{-1}$, and the self-consistent field cycle converges to $2.0 \times 10^{-6} \text{eV}$ [35]. The calculations of the electronic properties of the system are based on the optimized geometry.

The graphene $3 \times 3 \times 1$ supercell model constructed using MS is shown in figure 1(a). For a single crystal of graphene, a total of 20 atoms, which is marked with a thick line in the figure, and the serial number of each C atom is indicated in figure 1(b), with the Wyckoff positions of the C atom in the graphene geometry is 6k. The method of applying uniaxial tension and compression deformation is to apply only the transverse deformation to the graphene cells. Figure 2(a) shows the model for applying uniaxial tensile deformation, with a model for under uniaxial compression deformation in figure 2(b); The method of applying biaxial tension and compression deformation is to apply deformation to the graphene cells in two directions, the deformed model is shown in figure 3. In order to prevent the optimization of the structure from affecting the degree of deformation, 3-5 atoms in the deformed graphene structure are fixed. In the figure, $c_0$ and $c$ respectively represent the lattice length of the graphene primary cell and the tensile or compressed graphene lattice length. For the tensile and compressive deformation of graphene, this paper uses the deformation $\varepsilon$ to characterize, define it as $\varepsilon = (c-c_0)/c_0$, which is the percentage of graphene lattice tensile length and original lattice length.

3. Calculation results discussion

3.1. Structural optimization and structural stability

Firstly, the intrinsic graphene of $1 \times 1 \times 1$ is optimized. The lattice constant of the optimized graphene $a = 0.690 \text{nm}$, which the error is only 0.5% and 0.1% compared with the lattice constant of 0.686 nm measured by the experiment [36] and 0.689 nm obtained by simulation [37]. Next, the structural optimization calculation is performed on the model of the deformed graphene. When the graphene is subjected to tensile and...
Figure 1. Graphyne model.

Figure 2. Graphyne deformation diagram: (a) Uniaxial tensile model; (b) Uniaxial compression model.

Figure 3. Graphyne deformation diagram: (a) Biaxial tensile model; (b) Biaxial compression model.
compressive deformation, the sides of the hexagon in the structure are always kept straight, with the carbon atom plane deformed, but the connection bonds are intact during the calculation and the structure remains stable. The binding energy of the system can partially reflect the structural stability of the system. Therefore, we calculated the binding energy $E_b$ of the graphyne. The calculation formula \[ E_b = -(E_{\text{total}} - n_c E_c) \] is:

In the formula, $E_{\text{total}}$ is the total energy of the system, $E_c$ is the energy of a single carbon atom, and $n_c$ is the number of carbon atoms in the original cell.

Table 1 shows the binding energies of different tensile deformation graphyne systems and plots them as a curve, as shown in figure 4. The effect of tensile deformation on the binding energy of graphyne is studied under uniaxial and biaxial tensile deformation. It can be seen from the combination figure and table that the uniaxial and biaxial deformations are applied to the graphyne, the system binding energy decreases as the deformation increases. When the tensile deformation is small, the amount of binding energy change is small, and then the tendency to decrease becomes faster. When the compression deformation is small, the binding energy increases greatly, then increases slowly as the compression deformation increases. It indicates that the stability of the uniaxial and biaxial compression systems is high; however, the tensile deformation causes a decrease in the stability of the graphyne system. Compared with uniaxial, biaxial has a greater influence on the binding energy of graphyne.

The tensile deformation of the graphyne will inevitably affect the bond length of the graphyne. In order to analyze the status where bonding between carbon atoms in the graphyne structure, the charge density of the intrinsic graphyne is calculated as shown in figure 5. As shown in the same picture, closer to the color of red, the greater the charge density. It can be seen that the carbon atoms on the carbon chain are bonded in the form of a single bond and a triple bond ($\text{C} \equiv \text{C}$). The charge differential density of different tensile and compressive deformations is also performed later and is compared with the intrinsic graphyne results here.

The connecting bonds of the graphyne model have been numbered and shown in figure 6, discussing the bond length distribution of the graphyne structure. Table 2 shows the bond length of the intrinsic graphyne. It
can be seen that the length of the single bond on the carbon chain is 1.47 Å, which is shorter than the length of the conventional C–C single bond of 1.55 Å, and its consistent with the prediction of the literature [39] 1.46–1.48 Å. The length of the triple bond is 1.22 Å, which is slightly longer than the conventional C≡C triple bond 1.20 Å, which is the same as 1.22 Å calculated in literature [37, 38] and is close to 1.23 Å in literature [36]. We have measured the C–C bonds in the geometrically optimized tensile and compressive graphyne structure. The results are shown in figure 7. Figure 7(a) shows the relationship between the uniaxial tension and compression deformations and the bond length, and figure 7(b) shows the relationship between the biaxial tension and compression deformations and the bond length. It can be seen that all the two C–C single bonds in the system are much longer than the length of the acetyl bond, which are closed to the six-membered ring on the carbon chain. The bond length on the six-membered ring varies with the deformation.

The Mulliken bond order for graphyne is calculated in the paper. The graphyne is subjected to uniaxial deformation, while the deformation amount changes from −10% to 10%, and the length of each bond also changes. The change of the bond 1 on the six-membered ring is the most obvious, from 1.08 to 0.88, while the 5 bond is changes from 1.02 to 1.09. The single bonds 2 and 4 on the carbon chain changed slightly, decreasing

| Bond position | 1     | 2     | 3     | 4     | 5     |
|---------------|-------|-------|-------|-------|-------|
| Bond length   | 1.47  | 1.46  | 1.22  | 1.46  | 1.47  |

Figure 6. Carbon chain structure.

Figure 7. Bond length of graphyne: (a) Biaxial tensile; (b) Biaxial compression.
slightly from 1.01 to 0.88. The bond order of the C≡C triple bond is much higher than the other single bonds, which is slightly reduced from 2 to 1.94. The effect of biaxial deformation on the Mulliken bond order of the graphyne structure is analyzed. The single bond 5 on the six-membered ring is reduced from 1.08 to 0.96, the remaining bond length changes are roughly similar to the uniaxial. The results show that in the current range of deformation, the bond orders are all positive and the atoms form covalent bonds. The value of the bond order decreases as the deformation changes from −10% to 10%, and the covalent is weakened and the stability is reduced. This conclusion is consistent with the trend of binding energy. In the graphyne deformation system, the C–C single bond Mulliken bond order on the carbon chain is the smallest, which is the weakest chemical bond in the whole system, and it may be the key factor to improve the structural stability of the graphyne.

3.2. Effect of uniaxial tension and compression deformation on graphyne

The electronic properties of intrinsic graphyne and tensile deformation graphyne systems were calculated by CASTEP. The first Brillouin zone adopts a closed path $G(0,0,0) \rightarrow K(-0.333,0.667,0) \rightarrow M(0,0.5,0) \rightarrow G(0,0,0)$. The energy band structure and density of state of intrinsic graphyne calculated by the GGA and HSE06 methods are shown in figures 8(a) and (b) respectively. The shape and high symmetry point of the graphyne Brillouin zone are shown in figure 8(c). The results of figure 8(a) show that the intrinsic graphyne band gap appears at the M point of the Brillouin zone, and its value is 0.763 eV. It is indicated that the intrinsic graphyne established in this paper is a semiconductor of M direct transition in the Brillouin zone. The far right side of the figure is the total density of the states, which can be regarded as the projection of the band structure. It can be seen from the figure that the state density curve is in the valley position at the Fermi level, and its value is zero. The range of the zero region corresponds to the band gap of the band structure, which is 0.763 eV. However, it is well known that the band gap of semiconductor is underestimated by GGA. In contrast, hybrid functionals such
as HSE06 can reproduce the experimentally measured band gap quite well and give excellent description of the electronic structure of semiconductor. The HSE06 calculated band structure of graphyne is presented in figure 8(b). A 0.926 eV band gap is obtained, which is 0.163 higher than the GGA-PBE value. The error is only 0.21% compared with the 0.960 eV calculated in [32]. Compared with the GGA results, the band structure of GGA-PBE and HSE06 show similar characteristics except for the band gap, the band structures given by GGA-PBE and HSE06 exhibit similar features. Therefore we think that there are no obvious differences between the electronic properties calculated by these two functions, and all of the following results of this paper are obtained using GGA-PBE if not specified. The density structure of the states of the graphyne obtained by the two methods proves that the energy band structure of graphene has a large modification space and is more suitable for energy band engineering. This conclusion is consistent with the literature [28].

As can be seen from figure 9, when the stretched shape becomes 7.5% or less, the band gap is reduced from 0.763 eV to 0.394 eV, which always corresponds to a medium band gap semiconductor. When the tensile deformation increases to 10%, the band gap decreases to 0.123 eV constantly, which corresponds to the small band gap semiconductor. In the current studies, the band gap decreases as the degree of uniaxial tensile strain increases, which means that the minimum energy required for electrons in the valence band are excited to transition to conduction bands is reduced. From the density of states of different tensile deformations, it can be seen that the density of states of the system changes slightly with the change of the tensile deformation. The range in which the number of electronic states near the Fermi surface is zero decreases as the tensile deformation increases, and corresponds to the energy band structure.

Figure 9. (a)–(d) The band structure and DOS of graphyne with 2.5%, 5%, 7.5%, 10% deformation of uniaxial tensile.
Figure 10 represents the energy band and DOS of graphyne in uniaxial compression deformation at 2.5%, 5%, 7.5%, 10%. In contrast to uniaxial tensile deformation, the band gap value of uniaxial compression is positively correlated with the deformation, which means the stronger the degree of compression, the larger the band gap is. As the compression deformation changes from 2.5% to 10%, the band gap value increase constantly from 0.888 eV to 1.145 eV, and the density of states corresponds to the band structure. In the process of uniaxial deformation, both of them have direct band gap at point M, and the Fermi level has not move to conduction band or valence band.

In order to study the charge distribution and electron transfer, the differential charge density and Mulliken charge population of the graphyne uniaxial tension and compression systems are calculated. It can be used to measure the degree of density of the charge and the distribution of electrons. The uniaxial tensile and compression deformation graphyne systems differential charge density contour line are shown in figures 11 and 12. The charge populations of the C5, C6, C7, and C8 atoms of the graphyne under uniaxial deformation are listed in table 3.

Figures 11 and 12 indicate that the charge differential density of graphyne under different tensile and compressive deformations. Positive values in the scale means an increase in charge density, and negative values indicate a decrease in charge density. As can be seen from the figure, the differential charge distribution of graphyne is relatively local, mainly concentrated on the bond between the C–C atoms. There is a charge transfer phenomenon between the two C atoms, and the charge transfer between the two atoms C6 and C7 connected by the alkyne bond, which is particularly obvious. The uniaxial tensile deformation is applied to the graphyne, as
the deformation increases, the value of the partial charge accumulation of the alkyne bond between C6 and C7 decreases, and the electronegativity increases. Combined with the Mulliken charge population, it can be seen that the charge population values of C6 and C7 increased from 4.00 to 4.04, and the electrons lost 0.04e. It is consistent with the conclusions obtained from the charge differential density. Similarly, by analyzing the charge differential density of states under uniaxial compression deformation, it can be seen that the charge accumulation between the C6 and C7 atoms connected by the alkyne bond is intensified. It can be seen from the Mulliken charge population of the table that the compression deformation increases and the C atom obtains 0.02e of electrons. As the uniaxial tension and compression deformation increases, the electron transfer of the two C atoms connected by the alkyne bond is intensified. The larger the compression deformation, the more the electrons is obtained, and the larger the tensile deformation is, and the stronger the electron loss ability is.

### 3.3. Effect of biaxial tension and compression deformation on graphyne

Figure 13 and Figure 14 indicate that the band structure and DOS of graphyne under different tensile and compressive deformations. It can be seen that the band structure of the graphyne biaxial system is direct band

| Table 3. Mulliken charge population under uniaxial deformation. |
|-------------------|---|---|---|---|---|---|---|---|
| $\varepsilon/%$ | -10 | -7.5 | -5 | -2.5 | 0 | 2.5 | 5 | 7.5 | 10 |
| C5 | 4.04 | 4.03 | 4.02 | 4.01 | 4.00 | 3.99 | 3.99 | 3.98 | 3.97 |
| C6 | 3.98 | 3.98 | 3.99 | 3.99 | 4.00 | 4.01 | 4.01 | 4.03 | 4.04 |
| C7 | 3.98 | 3.98 | 3.99 | 3.99 | 4.00 | 4.01 | 4.01 | 4.03 | 4.04 |
| C8 | 4.04 | 4.03 | 4.02 | 4.01 | 4.00 | 3.99 | 3.99 | 3.98 | 3.97 |
gap, and the Fermi level has not move to conduction band or valence band. The intrinsic graphyne band gap is 0.763 eV. When the biaxial deformation is $-10\%$, which is the biaxial compression deformation becomes $10\%$, the band gap is only 0.349 eV. When the biaxial deformation is increased to $10\%$, which is the tensile deformation becomes $10\%$, the band gap is increased to 1.571 eV. It can be seen that under the biaxial deformation, the band gap becomes larger under the increasing deformation. The band gap values of the biaxial deformation and the uniaxial deformation calculated by the GGA and HSE06 methods are listed in table 4, and the band gap values of the them are changed into a graph, as shown in figure 15. The results show that uniaxial and biaxial tensile deformation have a great influence on the electronic structure of intrinsic graphyne. Its deformation has a linear correlation with the band gap value. Under uniaxial deformation, the deformation has a negative correlation with the band gap value, while under the biaxial deformation, a positive correlation exists with the band gap value. Comparing the two methods, it is found that the calculated value of the deformed graphyne using HSE06 method is significantly larger than that of GGA-PBE, but the band gap obtained by the them has the same trend with strain. Therefore, the electronic structures obtained by the two methods are essentially identical.

In summary, the deformation of the graphyne is equivalent to the application of an external force, and the resulting irregular movement of the atom causes the geometric symmetry of the support band being degenerate. The C–C orbital in the graphyne structure is re-hybridized, with the bond length in different directions changes, and the charge between atoms is redistributed, thus it leads to changes in the electronic structure of graphyne.
Figures 16 and 17 are charging difference on the density diagrams under different biaxial tensile and compressive deformations, and table 5 shows Mulliken charge populations of C5, C6, C7, and C8 atoms of graphyne under biaxial deformation. Combining figure and table for analysis, the results show that the charge transfer tendency of biaxial tensile and compression deformation is similar to that of uniaxial deformation. When the uniaxial and biaxial deformations are both tensile deformation, the C6 and C7 atoms on both sides of the acetyl bond lose electrons, the acetyl bond and its adjacent C5 and C8 get electrons, the electronegativity increases. When graphyne is subjected to compression deformation, C6 and C7 atoms acquire electrons, C5 and C8 lose electrons, and charge aggregation on acetyl bond. As the tensile and compressive deformations increase, charge transfer becomes intense. Compared with biaxial tension and compression, the severity of charge transfer

| Deformation:/% | −10 | −7.5 | −5 | −2.5 | 0 | 2.5 | 5 | 7.5 | 10 |
|----------------|-----|------|----|------|---|-----|---|-----|----|
| \(E_{\text{g}}(\text{GGA})/\text{eV}\) | 1.145 | 1.068 | 0.982 | 0.888 | 0.763 | 0.616 | 0.446 | 0.394 | 0.123 |
| \(E_{\text{g}}(\text{HSE})/\text{eV}\) | 0.349 | 0.45 | 0.552 | 0.663 | 0.763 | 0.929 | 1.083 | 1.279 | 1.571 |
| \(E_{\text{g}}(\text{HSE})/\text{eV}\) | 1.457 | 1.3268 | 1.219 | 1.144 | 0.926 | 0.822 | 0.735 | 0.651 | 0.563 |
| \(E_{\text{g}}(\text{HSE})/\text{eV}\) | 0.489 | 0.665 | 0.790 | 0.871 | 0.926 | 1.036 | 1.199 | 1.422 | 1.697 |

Figures 16 and 17 are charging difference on the density diagrams under different biaxial tensile and compressive deformations, and table 5 shows Mulliken charge populations of C5, C6, C7, and C8 atoms of graphyne under biaxial deformation. Combining figure and table for analysis, the results show that the charge transfer tendency of biaxial tensile and compression deformation is similar to that of uniaxial deformation. When the uniaxial and biaxial deformations are both tensile deformation, the C6 and C7 atoms on both sides of the acetyl bond lose electrons, the acetyl bond and its adjacent C5 and C8 get electrons, the electronegativity increases. When graphyne is subjected to compression deformation, C6 and C7 atoms acquire electrons, C5 and C8 lose electrons, and charge aggregation on acetyl bond. As the tensile and compressive deformations increase, charge transfer becomes intense. Compared with biaxial tension and compression, the severity of charge transfer
Figure 15. Band gap of deformation graphyne system.

Figure 16. (a)–(d) The differential charge density of graphyne with 2.5%, 5%, 7.5%, 10% deformation of biaxial tensile.

Figure 17. (a)–(d) The differential charge density of graphyne with −2.5%, −5%, −7.5%, −10% deformation of biaxial tensile.

Table 5. Mulliken charge population under biaxial deformation.

| ε/% | −10 | −7.5 | −5 | −2.5 | 0 | 2.5 | 5 | 7.5 | 10 |
|-----|-----|-----|----|------|---|-----|---|-----|----|
| C5  | 4.03| 4.02| 4.01| 4.01 | 4.00| 4.00| 3.99| 3.99| 3.98|
| C6  | 3.97| 3.98| 3.99| 3.99 | 4.00| 4.00| 4.01| 4.02| 4.03|
| C7  | 3.97| 3.98| 3.99| 3.99 | 4.00| 4.00| 4.01| 4.02| 4.03|
| C8  | 4.03| 4.02| 4.01| 4.01 | 4.00| 4.00| 3.99| 3.99| 3.98|
is sensitive to uniaxial changes and its effect is stronger than biaxial changes. There are three reasons for the change in charge distribution caused by strain. They are the change in the degree of orbital overlap, the covalency of the C atom bond, and the delocalized $\pi$ bond caused by the deformation. After the graphyne is subjected to tensile deformation, the bond length between the two C atoms increases, the degree of orbital overlap between the two atoms decreases, the atomic orbital decreases, the molecular orbitals are rearranged, and the electron is filled in the bond track. The calculation of the Mulliken bond order also shows the same conclusion. The bond order of the $C \equiv C$ triple bond connecting the C atom also decreases with the increase of the tensile deformation, the covalent is weakened, and the number of electrons in the orbit increases. The opposite is true when compressing, and the degree of orbital overlap becomes larger, the Mulliken bond order increases, the covalence increases, and the charge is more concentrated on the C atom. Li et al. [40] calculated the structural parameters of graphdiyne, and the calculating results indicated all the $\pi$-electrons of the carbons were able to form delocalized $\pi$-bonds and all the lengths of C-$\pi$-bonds were to become average. The change in bond length caused by deformation directly affects the structure of the delocalized $\pi$ electrons, especially the $C \equiv C$ triple bond connecting the C6 and C7 atoms. The conjugation of both the $\pi$ bonds which locate in horizontal and vertical to the graphyne plane makes the bond changed to be sensitive to deformation, so its electron transfer is more obvious.

4. Conclusion

Density functional theory is used to calculate the graphyne system under biaxial and uniaxial deformation. The binding energy, bond length and bond order are compared to study the effect of tensile and compression deformations on the stability of graphyne. The results show that the binding energy and bond order of graphyne are increased with the increase of compression deformation and decrease with the increase of tensile deformation, and stability is inversely related to the deformation. The effects of tensile and compressive deformation on the electronic structure are analyzed by studying its band structure, density of states, charge differential density and charge population. Energy band structure and density of states study show that the tensile and compression deformation does not change the direct band gap of the graphyne, and it cannot cause the Fermi level to move up and down, but has a regulatory effect on the band gap. The band gap decreases as the uniaxial deformations increases, widened as the biaxial deformations increases. In the current range of deformation, it always corresponds to the semiconductor and does not exhibit metallic properties. Comparing the energy band structure calculated by GGA and HSE06, the band gap value calculated by HSE06 method is larger, but the shape characteristics of the band structure are basically the same, and the band gap has the same trend with strain. The analysis of charge differential density and charge population show that when graphyne is subjected to tensile deformation, the C atoms on both sides of the acetyl bond lose electrons, the surrounding acetyl bond and C atom get electrons, the electronegativity increases. When graphyne is subjected to compression deformation, the C atoms on both sides of the acetyl bond get electrons, while the adjacent C atoms lose electrons, and the charge in the region where the acetyl bond is located gathers. As the tensile and compression deformations increase, the loss of electrons from the C atoms on both sides of the acetyl bond becomes severe. Comparing the effect of uniaxial and biaxial deformations on graphyne, it can be seen that compared with biaxial deformation, uniaxial deformation has lower sensitivity to the binding energy, bond order and band gap value of graphyne, and has a bigger influence on the degree of charge transfer.

Acknowledgments

This work was supported by the National Natural Science Foundation of China [Grant Number 51371049]; the Natural Science Foundation of Liaoning Province [Grant Number 20102173] and the Liaoning Provincial Department of Education Project [Grant Number LZGD2019003]

ORCID iDs

Lin Wei https://orcid.org/0000-0002-3473-389X

References

[1] Kroto H W, Heath J R, O’Brien S C, Curl R F and Smalley R E 1985 C60: buckminsterfullerene Nature 318 162–3
[2] Iijima S 1991 Helical microtubes of graphitic carbon Nature 354 56–8
[3] Novoselov K S, Geim A K, Morozov S V, Jiang D, Zhang Y, Dubonos S V, Grigorieva I V and Firsov A A 2004 Electric field effect in atomically thin carbon films Science 306 666–9
[4] Baughman R H, Eckhardt H and Kertesz M 1987 Structure–property predictions for new planar forms of carbon: Layered phases containing sp$^2$ and sp atoms Chem. Phys. 87 6687–99
[5] Li G, Li Y and Liu H 2010 Architecture of graphdiyne nanoscale films Chem. Commun. 46 3256–8
[6] Li Y, Xu L and Liu H 2014 Graphdiyne and graphyne: from theoretical predictions to practical construction Chem. Soc. Rev. 43 2572–86
[7] Zhou J, Gao X and Liu R 2013 Synthesis of graphdiyne nanowalls using acetylenic coupling reaction JACS 137 7596–9
[8] Wu B, Li M R and Xiao S N 2017 A graphyne-like porous carbon-rich network synthesized via alkynemetathesis Nano.尺度 9 11939–43
[9] Gao J, Li J and Chen Y 2018 Architecture and properties of a novel two-dimensional carbon material-graphitetrane Nano. Energy. 43 192–9
[10] Li G, Li Y and Qian X 2011 Construction of tubular molecule aggregations of graphdiyne for highly efficient field emission Phys. Chem. C 115 2611–5
[11] Chen J M, Xi Y, Wang D and Shuai Z G 2013 Carrier mobility in graphyne should be even larger than that in graphene: a theoretical prediction Phys. Chem. Lett. 4 1443–8
[12] Long M Q, Tang L, Wang D, Li Y L and Shuai Z G 2011 Electronic structure and carrier mobility in graphdiyne sheet and nanoribbons: theoretical predictions ACS Nano. 5 2593–600
[13] Ajori S, Ansari R and Mirnezhad M 2013 Mechanical properties of defective C$\gamma$-graphyne using molecular dynamics simulations Mater. Sci. Eng. A 561 34–9
[14] Mirnezhad M, Ansari R, Rohui H, Seif M and Faghihasar M 2012 Mechanical properties of two-dimensional graphyne sheet under hydrogen adsorption Solid State Commun. 152 1885–9
[15] Jafarzadeh H, Roknabadi M R, Shahrathaemiri N and Behdami M 2015 Electronic properties of C$\alpha$-graphyne nanoribbons under the electric field effect Physica E 67 54–8
[16] Lin Z Z, Wei Q and Zhu X 2014 Modulating the electronic properties of graphdiyne nanoribbons Carbon 2014 66 504–10
[17] Zhou Y H, Tan S H and Chen K Q 2014 Enhance the stability of C$\alpha$-graphyne nanoribbons by dihydrogenation Org. Electron. 15 5392–8
[18] Jang B, Koo J, Park M, Lee H, Nam Y, Kwon Y and Lee H 2013 Graphdiyne as a high-capacity lithium ion battery anode material Appl. Phys. Lett. 103 52–63
[19] Huang C H, Zhang S L, Liu H B, Han H, Li Y L and Shuai Z G 2011 Electronic structure and carrier mobility in graphdiyne sheet and nanoribbons: theoretical predictions Solid State Commun. 152 1885–9
[20] Huang C H, Zhang S L, Liu H B, Li Y J, Cui G L and Liu Y 2015 Graphdiyne for high capacity and long-life lithium storage Nano. Energy. 11 481–9
[21] Lee S H and Jhi S H 2015 A first-principles study of alkali-metal-decorated graphyne as oxygen-tolerant hydrogen storage media Carbon 81 418–25
[22] Liu Y, Liu W, Wang R G, Hao I F and Jiao W C 2014 Hydrogen storage using Na-decorated graphyne and its boron nitride analog Int. J. Hydrog. Energy. 39 12757–64
[23] Li J L, Gao Y H, Zhang Y and Cao J X 2014 Li decorated 6,6,12-graphyne: A new star for hydrogen storage material Int. J. Hydrog. Energy. 39 17112–7
[24] Wang Y S, Fei Yuan P, Li M, Feng Jang W, Sun Q and Jia Y 2013 Calcium-decorated graphyne nanotubes as promising hydrogen storage media: a first-principles study Solid State Chem. 197 323–8
[25] Xu B, Lei X L, Liu G, Wu M S and Ouyang C Y 2014 Li decorated graphyne as high-capacity hydrogen storage media: First-principles planar wave calculations 2014 Int. J. Hydrog. Energy. 39 17104–11
[26] Li R F, Ruo D W, Meng Z S, Zhang X B, Xu Z J, Liu Y Z, Xiao C Y and Deng K M 2013 Boron-substituted graphyne as a versatile material with high storage capacities of Li and H2:a multiscale theoretical study Physical Chemistry Chemical Physics Pccp. 15 16120–6
[27] Zhao W H, Yuan L F and Yang J L 2012 Graphdiyne as hydrogen purification membrane Chin. J. Chem. Phys. 25 344–40
[28] Balog R et al Bandgap opening in graphene induced by patterned hydrogen adsorption Nature Mater. 9 2010 315–9
[29] Ermos J, Weiss D et al 2005 Andreev reflection at high magnetic fields: evidence for electron and hole transport in edge states Physical Review Letters 95 107001
[30] Kim M, Safron N S, Han E, Arnold M S and Gopalan P 2010 Fabrication and characterization of large-area, semiconducting nanoporous graphene membranes Nano. Lett. 10 1125–31
[31] Yan X M 2011 Electronic structure and characteristics of bent graphene M. S. Dissertation (Wuxi) Jiangnan University
[32] Kand J, Li B, Wu F M et al 2011 Elastic, electronic, and optical properties of two-dimensional graphyne sheet Journal of Physical Chemistry C 115 20466–70
[33] Tang B, Luo Q, Zhang Q, Wu Z H and Ran Z L 2014 First principles study on the structure and electronic properties of P doped graphene Journal of Synthetic Crystals. 43 1269–73
[34] Perdew J P, Burke K and Ernzerhof M 1996 Generalized gradient approximation made simple Phys. Rev. Lett. 77 3865–8
[35] Liu G L, Zhou S and Fan D Z 2017 Effect of C$\gamma$ coverage on electronic structure and optical properties of graphene system Journal of Shenyang University of Technology, 39 622–8
[36] Huang C S and Li Y L 2016 Structure of 2D graphdiyne and its application in energy fields Acta Phys. Chim. Sin. 32 1314–29
[37] Zhao H, Zhou L N and Wei D J 2014 Lithium storage on extended graphenes: predicted by DFT calculations Chemical Journal of Chinese Universities. 8 1731–8
[38] Chen X, Cheng M J and Wu S Q 2017 First-principle study of structure stability and electronic structures of C$\gamma$ graphyne derivatives Acta Phys. Sin. 66 1070121–8
[39] Li Y J and Li Y L 2015 Two dimensional polymers—progress of full carbon graphyne Acta Polymerica sinica. 2 147–65
[40] Li X H, Wang X F and Li Z F 2013 Theoretical study on the structure and properties of graphdiyne Acta Chim. Sinica 71 75–80