A Study on Different Bandwidths and Rim Decorations’ Influence on the Mechanical Properties of Graphene Nanoribbon

Guo Ziliang*
School of Physics, Nankai University, Tianjin, China
*Corresponding author: 710160040@qq.com

Abstract. This paper structured the Graphene Nanoribbon with different bandwidths and rim decorations and obtained the ideal strength and modulus of elasticity based on the calculation under the First Principle. It can be known that the mechanical properties of Graphene Nanoribbon are close to that of graphene, which have less changes with different bandwidth. However, the mechanical properties would be influenced by different decorations which may change the electronic connection state of edge carbon atoms. The results found in this paper can provide some reference for researchers to study the mechanical properties of graphene nanoribbons in the future.

Keywords: the First-principles calculation, Graphene nanoribbons, rim decorations, bandwidth, modulus of elasticity, ideal strength

1. Introduction
In 2004, Konstantin Novoselov and AndreGeim from the University of Manchester in the UK used tape to tear the graphite [1] to obtain the "graphene" material that we are now familiar with. Before that, it was generally believed that materials with only a few atomic layers could not exist stably. However, with the discovery of graphene, it overturned this cognition, causing a great sensation.

Graphene nanoribbons are graphene ribbons with a width of less than 50 nm. Because of their excellent properties such as high conductivity and high thermal conductivity, they have great potential applications. The model of graphene nanoribbons was proposed by Fujita M et al as early as 1996 [2], but it was not until 2015 that Pascal Ruffieux and others synthesized graphene nanoribbons (ZGNRs) with serrated edges for the first time [3]. The width of graphene nanoribbons often affected its properties.

Low-dimensional materials are easy to break the mirror symmetry through rim decorations. Different groups are added to the hanging bonds on both sides to achieve the purpose of modification, which can break the symmetry of the material to obtain important properties such as piezoelectric and ferroelectric [4, 5]. Therefore, the modification of graphene nanoribbons is also a hot research question.

Besides its good electrical properties, graphene has the characteristics of high strength, high hardness [6] and high elastic modulus [7], and its maximum strain can also reach 25% [8]. When graphene turns into nanoribbons, its electrical and magnetic properties will change greatly due to the influence of edge states [9, 10]. Therefore, it is also a meaningful work to explore whether the mechanical properties of graphene nanoribbons will change.
To sum up, this paper structured the Graphene Nanoribbons with different bandwidths and rim decorations, which can be found in various studies frequently, calculated the ideal strength and modulus of elasticity under the First Principle, and compared the results. The obtained conclusion can offer reference for studies on graphene nanoribbons in the future.

2. Methods for calculation

2.1 Calculation parameters
This paper adopted VASP of the First Principle and density functional theory to calculate and described the interaction between electron and ion by projection augmented plane wave method (PAW), used to the PBE functional in the generalized gradient approximation (GGA) to deal with the exchange correlation energy between electrons. We set the truncation energy of plane wave to 500eV and pass-through Monkors-Park method in inverted space automatic generation 15 × 1 × 1 k-point grid sampling and adopted the convergence criterion of energy (EDIFFG=1e-6).

2.2 Implementation method
1) Modeling
The software Material studio was adopted to structure the Graphene nanoribbons, which had 6 carbon atoms for their width (N=6) and was modified with a hydrogen atom (CH-CH) for each side. See the Fig.1

Among them, the periodic direction is still the X axis, the vertical direction is the Y axis, and the direction of modification is the Z axis. This is the basic structure and the subsequent structural changes are based on this structure.

However, the vasp software can only calculate the 3D periodic materials. For the lower dimensional materials, a vacuum layer was needed to add to its periodic direction. We added a series of vacuum layers to Y-axis and Z-axis respectively, and found the appropriate vacuum layer by comparing the stress changes. We made the lattice length of Y-axis be 10Å, 15Å, and 20Å and the lattice length of Z-axis be 20.62Å, 25.62Å, 30.62Å, and 40.62Å. In order to obtain obvious comparison results, we selected the Nanoribbons before optimization, which can provide relatively large stress.

In order to explore the effects of different bandwidths and modifications of graphene nanoribbons on mechanical properties, we constructed the same modified N = 4, N = 8, N = 10 nanoribbons and different modified structures of N = 6. There were single hydrogen atom and double hydrogen atoms (CH-CH2) modified on both sides, single hydrogen atom and ether bond (CH-C2O) modified on both sides, and single hydrogen atom and hydroxyl group modified on both sides [14].

See the Fig.2-7

Fig. 1 CH-CH, N=6 structure
Fig. 2 CH-CH, N=4
Fig. 3 CH-CH, N=8
Fig. 4 CH-CH,N=10
As the object of vasp software was the constructed primitive cell, the calculated stress and elastic modulus must be processed:

\[ \sigma_{\text{true}} = \sigma \frac{W_Z W_Y}{h w} \]  
\[ C_{\text{true}} = C \frac{W_Z W_Y}{h w} \]  

Among them, \( \sigma \) represented the stress, \( C \) represented the elastic modulus, \( W_Z W_Y \) represented the thickness of vacuum layer in Y and Z axis, \( h \) represented the thickness of graphene, and we take \( h = 3.4 \) Å. \( w \) represented the bandwidth of graphene, which will change with different \( N \). Because different modifications have little effect on the width, we used the width of CH-CH structure to replace the width of all modifications.

See the Table 1

| \( N \) | \( w/\text{Å} \) |
|------|--------|
| 4    | 9.28   |
| 6    | 13.54  |
| 8    | 17.80  |
| 10   | 22.06  |

2) Mechanical calculation

The elastic properties of materials often show a linear relationship at small strain. Here follows the formula:

\[
\begin{bmatrix}
\sigma_1 \\
\sigma_2 \\
\sigma_3 \\
\sigma_4 \\
\sigma_5 \\
\sigma_6
\end{bmatrix} =
\begin{bmatrix}
C_{11} & C_{12} & C_{13} & C_{14} & C_{15} & C_{16} \\
C_{21} & C_{22} & C_{23} & C_{24} & C_{25} & C_{26} \\
C_{31} & C_{32} & C_{33} & C_{34} & C_{35} & C_{36} \\
C_{41} & C_{42} & C_{43} & C_{44} & C_{45} & C_{46} \\
C_{51} & C_{52} & C_{53} & C_{54} & C_{55} & C_{56} \\
C_{61} & C_{62} & C_{63} & C_{64} & C_{65} & C_{66} \\
\end{bmatrix}
\begin{bmatrix}
\epsilon_1 \\
\epsilon_2 \\
\epsilon_3 \\
\epsilon_4 \\
\epsilon_5 \\
\epsilon_6
\end{bmatrix}
\]  

Among them, \( C_{xy} \) represented the elastic modulus in the corresponding direction. For graphene nanoribbons, the strain and stress applied by us were along to the X-axis direction, i.e. 1 direction. In that condition, the elastic modulus we focused was \( C_{11} \). By setting IBRION = 6, we can use the direct method to calculate its elastic modulus.

The ideal strength was calculated by calculating the stress-strain relationship. The addition of strain was realized by increasing the lattice length in the corresponding direction, and the length in the direction was kept to be unchanged, relaxing atoms in the cell to obtain the stress. Balancing the calculation accuracy and time cost, it was set that NSW=3 after testing. When the strain was small, it often changed linearly, and its slope was \( C_{11} \) in equation (3). This method was considered as the method of indirect measurement of elastic modulus. We can use these two methods to measure \( C_{11} \) for comparison.

With the increase of strain, the stress reached the maximum and then decreased. At this time, we believed that the maximum stress is the ideal strength. When calculating the strain, it can be set that IBRION=2.

3. Results

3.1 Selection of vacuum layer

Comparing the stresses of different vacuum layers in the Y-axis and Z-axis directions, the same parts in equations (1) and (2) were not considered.

See the Table 2, 3
Table 2 Relationship between Y-axis vacuum layer and calculation results

|       | 10             | 15             | 20             |
|-------|----------------|----------------|----------------|
| $\sigma_1$/kbar | -105.75361     | -70.58559      | -52.96131      |
| $C_{11}$/kbar   | -1806.5525     | -1203.4123     | -902.6802      |
| $\sigma_1W_Y$  | -1057.53       | -1058.78       | -1059.22       |
| $C_{11}W_Y$     | -18065.52      | -18051.15      | -18053.60      |

Table 3 Relationship between z-axis vacuum layer and calculation results

|       | 20.62          | 25.62          | 30.62          | 40.62          |
|-------|----------------|----------------|----------------|----------------|
| $\sigma_1$/kbar | -104.85741     | -84.40547      | -70.58559      | -53.17616      |
| $C_{11}$/kbar   | -1800.5167     | -1437.9011     | -1203.4123     | -908.0650      |
| $\sigma_1W_Z$  | -2162.01       | -2162.46       | -2161.33       | -2160.01       |
| $C_{11}W_Z$     | -37126.52      | -36838.99      | -36848.48      | -36885.60      |

Therefore, we selected $W_Y$ to be 20Å and $W_Z$ to be 40.62Å, which can make the vacuum layer large enough for ensuring the correct calculated result.

3.2 Calculation results of basic structure

The calculation result of basic structure of CH-CH, N=6 was showed in the chart without considering the sign of data. Because large strains are involved, the real strain was defined as

$$\varepsilon = \int_{l_0}^{l} \frac{dt}{l} = \ln \frac{l}{l_0}$$

where $l$ represented the current length of the lattice and $l_0$ represented the initial length of the lattice.

The Fig. (8) is the stress-strain curve and the Fig. (9) showed the results of linear fitting of strain and stress at small strain, with the slope as the modulus of elasticity.

![Fig. 8 CH-CH, N=6 stress-strain relationship](image1)

![Fig. 9 CH-CH, N=6 small strain linear fitting](image2)

Table 4 Ideal strength and elastic modulus of CH-CH, N=6

|                  | ideal strength | Direct calculated $C_{11}$ | Indirect calculated $C_{11}$ |
|------------------|----------------|----------------------------|------------------------------|
| Calculated value/kbar | 70.46686 | 555.8541                  | 556.05735                    |
| True value/kbar   | 1232.5118     | 9722.2547                 | 9725.8097                    |
| True value/Gpa    | 123.2512      | 972.2255                  | 972.5810                     |

From the Table 4, it can be seen that the elastic modulus calculated by the two methods is very close. As a result, the following elastic modulus can be calculated by indirect method.

Based on the Table 4, it can be found that if N=6, the elastic modulus of graphene nanoribbons modified by hydrogen atom was about 0.972Tpa, and the ideal strength was about 123.25Gpa. The maximum strain before fracture was 0.25[6, 7, 8]. These data are very close to graphene. Therefore, we can know that the mechanical properties of graphene nanoribbons in the periodic direction are similar to that in graphene, and the edge state has little effect on it.

Additionally, we can also use ideal strength to calculate the fracture surface energy of nanoribbons, as mentioned below [15].
\[ \sigma = \frac{\gamma C}{a} \]  

Among them, \( \sigma \) was the ideal strength, \( C \) was the elastic modulus, \( \gamma \) was the surface energy, and \( a \) was the initial lattice length, which was 2.45Å. \( 2\gamma = 38.13 \times 10^{-4}\text{J/m}^2 \) can be obtained if bring in the data.

3.3 Influence of width

For the calculation of different widths of CH-CH structure, the values of strain in the range of 0.15-0.32 were taken for drawing, see the Fig.10-13.

![Fig. 10 N=4](image1)

![Fig. 11 N=6](image2)

![Fig. 12 N=8](image3)

![Fig. 13 N=10](image4)

Then, the stress-strain fitting diagram of small strain of each width was made, see the Fig.14-16.

![Fig. 14 N=4](image5)

![Fig. 15 N=8](image6)

![Fig. 16 N=10](image7)

**Table 5** Ideal strength and elastic modulus of nanoribbons with different widths

|               | N=4      | N=6      | N=8      | N=10     |
|---------------|----------|----------|----------|----------|
| Calculated value of ideal strength /kbar | 47.9794  | 70.4668  | 90.1092  | 110.9491 |
| True value of ideal strength /Gpa         | 122.442  | 123.251  | 119.888  | 119.109  |
| Calculated value of elastic modulus /kbar | 362.66   | 556.06   | 717.73   | 893.22   |
| True value of elastic modulus /Gpa         | 925.50   | 972.59   | 954.92   | 958.91   |

According to the Table 5, we can know that, firstly, within this width change, all mechanical property indexes were close to each other, reaching the ideal strength at the strain of about 0.25, and the ideal strength and elastic modulus were relatively close. However, through careful comparison, it can be found that the ideal strength and elastic modulus reached the maximum at \( N = 6 \), and then decreased with the increase of width. But if \( N = 4 \), it was small than \( N = 6 \). And the stress-strain diagram of \( N = 4 \) was flatter compared with the other three, which showed that \( N = 4 \) is special. We speculated that when \( N \leq 4 \), the mechanical properties of nanoribbons are affected by the fine width.
3.4 Influence of decoration

We made stress-strain diagrams respectively based on different modified structures, see the Fig.17-20

![Fig. 17 CH-C2O](image1)

![Fig. 18 CH-CH](image2)

![Fig. 19 CH-CH2](image3)

![Fig. 20 CH-CHO](image4)

Then, the small strain stress-strain fitting diagram of each modified structure was made, see the Fig.21-23

![Fig. 21 CH-C2O](image5)

![Fig. 22 CH-CH2](image6)

![Fig. 23 CH-CHO](image7)

Table 6 Ideal strength and elastic modulus of nanoribbons with different rim decorations

|                         | CH-C2O  | CH-CH   | CH-CH2  | CH-CHO  |
|-------------------------|---------|---------|---------|---------|
| Calculated value of ideal strength /kbar | 65.1285 | 70.4668 | 62.7334 | 69.3395 |
| True value of ideal strength /Gpa       | 113.91  | 123.25  | 109.72  | 121.28  |
| Calculated value of elastic modulus /kbar| 501.04  | 556.06  | 509.77  | 561.74  |
| True value of elastic modulus /Gpa      | 876.35  | 972.59  | 891.62  | 982.52  |

Based on the Table 6, we can find that for both elastic modulus and ideal strength, the CH-CH was close to the CH-CHO, and the CH-CH was close to CH-C2O. It is known that the edges C of first two structures were the hybrid sp², which had a suspension electron. The latter two structures had suspended electrons in the sub outer C atom [14]. We speculated that the connection between the outermost carbon atom and the inner carbon atom of the latter two structures became weaker due to the loss of the original hanging electrons in the outermost carbon. In that condition, the ideal strength and elastic modulus of the latter two structures were less than those in the state with the suspended electrons in the outermost carbon. From this, we can know that the electron distribution structure will have a certain impact on its mechanical properties.

4. Conclusion

Graphene nanoribbons with different bandwidths and rim decorations were structured in this paper.
Firstly, the selection of vacuum layer was explored to select the vacuum layer with appropriate thickness. Then, it made a calculation on the basic structure of CH-CH, N=6, and compared the results with the Graphene, finding that both mechanical properties are close, which can be considered as a support for the application of graphene nanoribbons in the future. Besides that, surface energy of graphene nanoribbons was calculated based on ideal strengths, which can be excavated more.

We also calculated the ideal strength and modulus of elasticity of Graphene nanoribbons with different bandwidths and different modifications. After comparison, we found that bandwidth has little effect on its mechanical properties, which would dispel misgivings when applying Graphene Nanoribbon with different bandwidths. However, when N≤4, it should be noticed that too fine nanoribbons may have some unexpected problems. The rim decorations have a certain effect on the mechanical properties of nanoribbons. If the electronic connection status are not changed between Graphene nanoribbons, only changing the modified functional groups, the fluences would be very small. Moreover, if the rim decorations changed the electronic connection between carbon atoms, the mechanical properties will change obviously, which can provide a reference for future studies on different modified graphene nanoribbons.

References
[1] Novsclov K S, Geim A K, Morozov S V et al. Electric field effect in atomically thin carbon films[J]. Science, 2004, 306(5696): 666-669.
[2] Fujita M., Wakabayashi K., Nakada K. and Kusakabe K. Peculiar Localized State at Zigzag Graphite Edge[J]. Journal of the Physics Society Japan, 1996, 65(7): 1920.
[3] P. Ruffieux, S. Wang, B. Yang, C. S. nchez-S. nchez, J. Liu, T. Dienel, L. Talirz, P. Shinde, C. A. Pignedoli, D. Passerone, T. Dumslaff, X. Feng, K. Mü llen, R. Fasel, on-surface synthesis of graphene nanoribbons with zigzag edge topology, Nature, 531 (2016) 489-492.
[4] M. Wu, J.D. Burton, E.Y. Tsymbal, X.C. Zeng, P. Jena, Hydroxyl-decorated graphene systems as candidates for organic metal-free ferroelectrics, multiferroics, and high-performance proton battery cathode materials, Physical Review B, 87 (2013) 081406.
[5] L. onsager, Crystal Statistics. I. A Two-Dimensional Model with an order-Disorder Transition, Physical Review, 65 (1944) 117-149.
[6] Yu V, Hilke M. Large contrast enhancement of graphene monolayers by angle detection[J]. Applied Physics Letters, 2009, 95(15): 151904.
[7] Lee C, Wei X, Kysar J W, et al. Measurement of the elastic properties and intrinsic strength of monolayer graphene [J]. Science, 2008, 321(5887): 385-388.
[8] Tomori H, Kanda A, Goto H, et al. Introducing nonuniform strain to graphene using dielectric nanopillars[J]. Applied Physics Express, 2011, 4(7): 075102.
[9] Lin L, Zhang J C, Su H S, et al. Towards super-clean graphene [J]. Nature Communications, 2019, 10(1): 1912.
[10] Gonzalez — Herrero H, Gomez-Rodriguez J M, Mallet P, et al. Atomic-scale control of graphene magnetism by using hydrogen atoms[J]. Science, 2016, 352(6284): 43-7-441.
[11] G. Kresse, J. Hafner, Ab initio molecular dynamics for liquid metals, Physical Review B, 47 (1993) 558-561.
[12] J.P. Perdew, K. Burke, M. Ernzerhof, Generalized Gradient Approximation Made Simple, Physical Review Letters, 77 (1996) 3865-3868.
[13] K. Nakada, M. Fujita, G. Dresselhaus, M.S. Dresselhaus, Edge state in graphene ribbons: Nanometer size effect and edge shape dependence, Physical Review B, 54 (1996) 17954-17961.
[14] G. Lee, K. Cho, Electronic structures of zigzag graphene nanoribbons with edge hydrogenation and oxidation, Physical Review B, 79 (2009) 165440.
[15] Zhaoxian Xiong. Introduction to Material Physics [M]. Beijing: Science Press, 2012: 12