A density functional theory study on thermal properties of perfect and defective graphene

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Abstract: In present work, the graphene with various defects have been investigated by First-principles based on DFT, and the properties are compared to perfect graphene. The calculated results show that the topological structure exhibits the minimum defect formation energy, which will be the easiest defective structure to form. The Perfect graphene, Single-vacancy graphene and Double-vacancy graphene exhibit metallicity, but the electrical conductivity of Perfect graphene is not as good as vacancy defective graphene. The Topology graphene is semiconductor. Single-vacancy defect emerging in graphene will pin the C atoms along with the vacancy. The C atoms closest to vacancy is easy to loosen in Double-vacancy graphene. The Topology graphene is comparatively stable in defective graphene.

1. Introduction

Graphene, the two-dimensional carbon film was firstly obtained by Geim et al. [1] in 2004. It has aroused tremendous research interests for distinct and remarkable mechanical, electronic and thermal properties and has been applied in lots of fields, such as physics, chemistry and materials science [2]. Graphene also exhibits some defects which can be observed by high resolution transmission electron microscopy (HRTEM) [3]; and, similar, these defects can be widely used in particular engineering applications.

The defects in graphene have significant effect on microstructure and properties of graphene. Experimental and theoretical investigations carried out by Banhart et al. [4] show that the graphene exhibits defect will modify the chemical and electronic properties. Palacios et al. [5] confirmed that the defective graphene plays an important role in the development of future communication applications. Gao et al. [6] illustrate that the imperfect graphene exhibits the potential to impact electronic properties of graphene-based semiconductors. Taluja et al. [7] applied defects in graphene to the supercapacitors because of electronic properties.

However, the investigation of monolayer graphene is hard to implement, because the pristine graphene with the defect is hard to construct in laboratory. A theoretical calculation based on density functional theory (DFT) can be performed to help researchers understand the structure and physical or chemical properties. In present work, the graphene with various defects have been investigated by First-principles based on DFT, and the properties were compared to perfect graphene.
2. Calculation method and details

The calculations in this work were all performed by DFT using the CASTEP Code [8]. The interactions between the ionic cores and the valence electrons were described by the plane-wave ultrasoft pseudopotential method [9]. Furthermore, the 2p² for C were chosen as the valence electrons of the atoms. The PW91 [10] and PBE [11] functional of GGA and LDA [12,13] were utilized to treat the exchange-correlation interactions. The Brillouin zone was sampled by means of the Monkhorst-Pack k-point grid using a grid from 3×3×1 to 11×11×11 for perfect and defective graphene model. A kinetic energy cutoff value was filtrated from 300 eV to 800 eV for perfect and defective graphene. For obtaining well-formedness of perfect and defective graphene, the BFGS algorithm [14] was applied to geometry optimization to reach the ground state. The following convergence parameters were set in the calculations: the total energy tolerance was 1.0 ×10⁻⁵ eV/atom, the maximum force tolerance was 0.03 eV/Å, the stress on each atom was 0.05 GPa, and maximal displacement was 0.001 Å.

3. Results and discussions

3.1. Perfect monolayer graphene

In order to evaluate the rationality and accuracy, a suit of accurate and efficient parameters for monolayer graphene were designed. The perfect monolayer graphene exhibits a hexagonal two-dimensional atomic grid structure caused by the sp² hybrid orbitals of carbon atoms.

![Fig. 1 Convergence curves of monolayer graphene (a) according to cutoff energy (k-points: 6×6×1) (b) according to k-points (energy cutoff: 550 eV)](image)

Generally, the denser the k-point grid is and the greater the energy cutoff \(E_{\text{cut}}\) is, the more accurate the simulation of total energy will be. The results of convergence test are plotted in Figure 1, which indicates that the lattice parameters of monolayer graphene will tend to converge when \(E_{\text{cut}}\) is programmed to 550 eV and k-point is programmed to 6×6×1. The efficiency of simulation will slump with increasing \(E_{\text{cut}}\) and k-point. Therefore, the setup parameters for monolayer graphene are identified as 6×6×1 (k-point grid) and 550 eV \(E_{\text{cut}}\).

| Data source | PBE | PW91 | LDA |
|-------------|-----|------|-----|
| This work   | 2.4623 | 2.4612 | 2.4651 |
| Other calc. | 2.47 \([15]\) | 2.459 \([16]\) | 2.46 \([17]\) |
| Expt.       | -- | -- | 2.460 \([15]\) |

On the process of geometry optimization, the most common functional of exchange-correlation are LDA and GGA. Generally, the PW91 and PBE are always regarded as an accurate approximation among GGA. The lattice parameter of monolayer graphene was simulated by above approximation method. The results of the lattice parameters of monolayer graphene are listed in Table 1, which are compared
with other calculations and experiment. Therefore, energy cutoff (550 eV), k-point (6×6×1) and exchange-correlation interaction (PW91) were programmed in subsequent investigation, which can provide enough accuracy and efficiency.

3.2. Defective graphene
In the process of establishing three kinds of defect model, defect concentration and the limitation of the calculated amount are considered. In this paper, the Single-vacancy defect, Double-vacancy defect and the Topology defect are established on the supercell of the intrinsic graphene. The model size of defective graphene is based on non-deformation of the original supercell edge causing by introducing defects. The Perfect graphene and three kinds of defective graphene, which are called Single-vacancy, Double-vacancy and Topology for short, are shown in the Figure 2.

![Fig. 2 Variously defective graphene models (a) Perfect graphene, (b) Single-vacancy, (c) Double-vacancy, (d) Topology](image)

3.2.1. Defect formation energy
The defect formation energy $E_{\text{def}}$ is the difference between the total energy of the defective system and the total energy of the perfect system. According to this method, the deduced defect formation energies are shown in Table 2. It is obvious that the graphene with various defects are unstable because of the positive energy. However, the topological structure exhibits the minimum defect formation energy, which will be the easiest defective structure to form, comparatively.

| Graphene models  | $E_{\text{tot}}$ (eV) | $E_{\text{def}}$ (eV) |
|------------------|----------------------|-----------------------|
| Perfect graphene | -15192.0177          |                       |
| Single-vacancy   | -15027.0311          | 164.9866              |
| Double-vacancy   | -14872.5272          | 319.4905              |
| Topology         | -15185.0378          | 6.9799                |

3.2.2. Band structure and DOS
When studying the band structure, the energy bands away from the Fermi level are ignored. Only about 30 energy bands around the Fermi level are selected to investigate. As shown in Fig. 3a), it is observed that the valence band maximum and the conduction band minimum are located at the F point of the Brillouin zone. The band gap in band structure of Perfect monolayer graphene is zero, which is identified that the Perfect monolayer graphene exhibits metallicity with a zero bandgap. When vacancy emerges in graphene as show in Fig. 3b) and 3c), the valence band maximum and the conduction band minimum intersect. The Single-vacancy and the Double-vacancy graphene exhibit strong metallicity. However, the energy gap of Topology is opened. The energy gap is 0.21 eV, which identify that the Topology become semiconductor compared with other graphene.

Figure 4 shows the DOS (partial and sum) of the graphene with various defects. As Figure 4 a) shown, the DOS at the Fermi level is zero, that it corresponds to the result of band structure. The band in the range from -20 eV to -3 eV for Perfect graphene is from C 2p and C 2s orbitals. The contribution of C
2p orbital increases, while that of C 2s orbital decrease with the increase of the energy from -20 eV to -3 eV. The band between -3 eV and 7 eV is mainly from C 2p orbital. Above 7 eV both the C 2p and C 2s orbitals contribute to Perfect graphene again. After the vacancy emerging in graphene, the contribution of C 2s orbitals increase. In order to hold the defective graphene steady, the region of C 2s orbitals have to increase. In addition, there is no bandgap in Single-vacancy and the Double-vacancy, which identify that the graphene with vacancy defects exhibit strong metallicity. The DOS of Topology is plotted in Figure 4 d), the biggest transformation also emerge in Fermi level, which declaim that the density of states at the Fermi level is zero when graphene form the topological structure. The energy gap is wider than others, the character of semiconductor is verified again. The contribution of C 2s orbitals from -7 eV to 7 eV vanish because of more stable structure of Topology than vacancy graphene.

![Fig. 3 Band structure of a) Perfect graphene, b) Single-vacancy, c) Double-vacancy, d) Topology](image)

![Fig. 4 DOS of a) Perfect graphene, b) Single-vacancy, c) Double-vacancy, d) Topology](image)
3.2.3. Atomic orbital population and bond overlap population

The distribution, transfer and bonding of charge in crystal can be declared by analyzing atomic orbital population. The atomic orbital population of the graphene with various defects are shown in Table 3. Comparing the Single-vacancy to the Perfect graphene, the total charge of C atoms closest to vacancy get 0.02 charge. A lot of charge located on 2p orbital transfers to 2s orbital, the interaction between atoms weaken. The transfer of charge substantial decline, relatively, from 2p orbital to 2s orbital; and the interaction gradually recover to the normal state of Perfect graphene. As for the others, the charge is unchanged. It suggests that the effect of Single-vacancy is short-range. Comparing to the Perfect graphene, the total charge of C atoms closest to vacancy in Double-vacancy lose 0.02 charge. The charge located on 2p orbital transfers to 2s orbital, but transfers not as much as that closest to vacancy in Single-vacancy. The total charge of C atoms next-closest to vacancy in Double-vacancy has no change. There is no obvious change on other C atoms comparing to Perfect graphene. It suggests that the effect of Double-vacancy is also short-range. But the effect is greater than Single-vacancy defect.

| Graphene models     | Species                    | s   | p   | Total | Charge |
|---------------------|----------------------------|-----|-----|-------|--------|
| Perfect graphene    | C                          | 1.05| 2.95| 4.00  | 0.00   |
| Single-vacancy      | C (closest to vacancy)     | 1.16| 2.82| 3.98  | 0.02   |
|                     | C (next-closest to vacancy)| 1.06| 2.93| 3.99  | 0.01   |
|                     | C (others)                 | 1.05| 2.95| 4.00  | 0.00   |
| Double-vacancy      | C (closest to vacancy)     | 1.12| 2.91| 4.02  | -0.02  |
|                     | C (next-closest to vacancy)| 1.10| 2.91| 4.00  | 0.00   |
|                     | C (others)                 | 1.04| 2.96| 4.00  | 0.00   |
| Topology            | C (5-7-7)                  | 1.06| 2.91| 3.97  | 0.03   |
|                     | C (5-6-7)                  | 1.05| 2.97| 4.02  | -0.02  |
|                     | C (5-6-6)                  | 1.03| 2.95| 3.98  | 0.02   |
|                     | C (6-6-7)                  | 1.07| 2.94| 4.01  | 0.01   |
|                     | C (others)                 | 1.05| 2.95| 4.00  | 0.00   |

Topology exhibits two 5-membered rings and two 7-membered rings. In order to understand the different positions of C atoms, the C atoms are marked according to the polygon of three adjacent rings as show in Fig. 5. Throughout all the C atoms in Topology as Tab. 3 stating, comparing to transfer of charge in Single-vacancy and Double-vacancy, only a little charge located on 2p orbital transfers to 2s orbital. Even more, the charge of C atoms closest to above marked C atoms is same to that in Perfect graphene. It follows that the C atoms in Topology are more stable than other structures, because there is no broken bond emerging.

The overlap of electron cloud between two bonded atoms can be expressed by bond overlap populations; and then the bond length and strength between atoms can bedeclaimed through the bond overlap populations. The greater the bond overlap populations, the stronger the bond. The bond overlap populations of variously defective graphene are shown in Table 4. Both the bond overlap populations closest to vacancy and next-closest to vacancy in Single-vacancy are stronger than that in Perfect graphene. It is indicated that the vacancy defects in Single-vacancy exhibit extremely pinning effect.
Therefore, one vacancy defect emerging in graphene will pin the C atoms along with the vacancy. Although the bond overlap populations closest to vacancy in Double-vacancy is more than that in Perfect graphene, the bond overlap populations next-closest to vacancy is less than that in Perfect graphene. It is indicated that, the C atoms closest to vacancy is easy to loosen, because Double-vacancy defect will destroy the stability of the graphene structure.

The bond overlap populations in Topology exhibit versatility. The 7-membered rings and the 5-membered rings as marked in Figure 5 are greatly affected because of the changes of six carboatomic ring. At the same time, the C atoms near to the 7-membered rings and the 5-membered rings are also implicated. The bond overlap populations between C (5-7-7)-C (5-7-7)-C (6-6-7)-C (5-6-7)-C (5-6-7)-C (5-7-7) in 7-membered rings are 1.11, 1.01, 1.07, 1.03, 1.07 and 1.01 respectively. The bond overlap populations between C (5-7-7)-C (5-6-7)-C (5-6-6)-C (5-6-6)-C (5-7-7)-C (5-6-7) in 5-membered rings are 1.01, 1.10, 1.07, 1.10 and 1.01 respectively. Comparing to these bond overlap populations, the population between C (5-7-7)-C (5-6-7) located in a 7-membered ring and a 5-membered ring simultaneously is far less than that in Perfect graphene because of the interaction between C (5-7-7)-C (5-7-7) in a 7-membered ring and C (5-6-7)-C (5-6-6) in a 5-membered ring. Therefore, this bond is the weakest compared to all above bands in variously defective graphene. In addition, the 5-membered rings are more stable than the 7-membered rings. The bond overlap populations next-closest to above 7-membered rings and 5-membered rings are 1.06, 1.07 and 1.08, respectively, which reveal that these C atoms near to the metatypical rings has a little influence. The Topology is comparatively stable in the graphene with various defects.

| Tab. 4 Bond overlap population of variously defective graphene |
|---------------|---------------|---------------|
| Bond          | Populations   | Length (nm)   |
| C-C           | 1.07          | 0.1426        |
| C-C (closest to vacancy) | 1.19          | 0.1387        |
| C-C (next-closest to vacancy) | 1.11          | 0.1409        |
| C-C (others)  | 1.07          | 0.1424        |
| C-C (5-7-7)-C (5-7-7) | 1.12          | 0.1374        |
| C-C (5-6-7)-C (6-6-7) | 1.04          | 0.158         |
| C-C (6-6-6)-C (6-6-6) | 1.07          | 0.1420        |
| C-C (others)  | 1.07          | 0.1420        |
| C-C (6-6-7)-C (6-6-6) | 1.07          | 0.1427        |

4. Conclusion
The topological structure exhibits the minimum defect formation energy, which will be the easiest defective structure to form. The Perfect graphene, Single-vacancy graphene and Double-vacancy graphene exhibit metallicity, but the electrical conductivity of Perfect graphene is not as good as vacancy defective graphene. The Topology graphene is semiconductor. Single-vacancy defect emerging in graphene will pin the C atoms along with the vacancy. However, the C atoms closest to vacancy is easy to loosen in Double-vacancy graphene. The Topology graphene is comparatively stable in defective graphene.

Acknowledgments
The authors acknowledge the financial support from the Research capacity cultivation Fund of Shenyang University of Technology (Grant No. 200005742).
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