Strain-induced modulation of mechanical properties and electronic structure of edge-modification graphene nanoribbons

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***Abstract*—The mechanical properties and electronic structure of graphene nanoribbons(GNRs) which modified atoms or molecular groups on the zigzag edges can be tuned under the uniaxial tensile strain for application on the electronic devices. We study the elastic and plastic deformation of GNRs. The modified zigzag edges play a key role in tense force, elastic constant, critical point (the critical point of elastic and plastic deformation) and the energy gaps. In particular, it is shown that the energy gap of edge-modification GNRs can be strongly modified under uniaxial tensile strain. This way, offer new opportunities to electronic transport and force-electronic devices for next-generation electronics.**

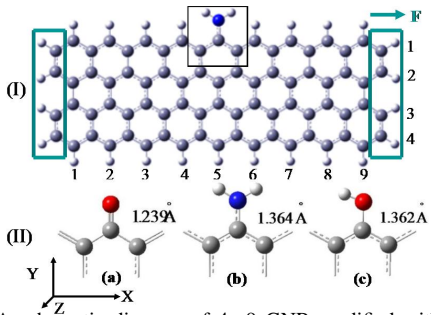

Fig. 1. (I) A schematic diagram of 4×9 GNR modified with NH_2 at the 5 site at zigzag edge; (II) Local structure of edge-modification GNRs. The zigzag edge modified with O, NH_2 and OH in (a), (b) and (c),respectively.

I. Introduction

Due to the graphene nanoribbons (GNRs) have capabilities to continuously control the band gap, it can be expected the candidates for future electronic and optoelectronic devices[1]. However, GNRs can not be produced in the same condition, a variety of lithographic fabrication (e.g oxygen plasma) are modified with oxygen at edge. In addition, diverse atoms or molecular groups may be introduced in the manufacturing process (e.g NH_2 and OH). Some theoretical and experimental studies have proved that local and uniform strain can tune the electronic properties and transport characteristics of GNRs[2], [3]. Therefore, it is vital to study the mechanical properties and electronic structure of edge-modification GNRs by the uniaxial tensile strain.

In order to describe the pristine GNRs, we discusse the mechanical properties and electronic structure of GNRs which are modified with H, O, OH and NH_2 at zigzag edges (because the zigzag interface is relatively more prone to atoms or molecular groups adsorbed). We investigate geometric and electronic properties of GNRs by the uniaxial tensile strain. We find that tension force F_T, elastic constant C and critical point (the critical point of elastic and plastic deformation) of GNRs are depend on the modified edge. Furthermore, the energy gaps of GNRs change dramatically under uniaxial strains.

II. METHODS

The electronic structure calculations are performed using the density-functional theory (DFT) by PAW potentials[4]. The exchange and correlation effects of the electrons has been approximated by Generalized Gradient Approximation (GGA), as implemented in Vienna Ab initio Simulation Package (VASP)[5]. The geometry are optimized with the conjugate-gradient algorithm method. All structures are treated within supercell geometry using the periodic boundary conditions. The size of supercells are carefully tested to maintain a sufficiently large separation between adjacent nanoribbons (>12Å form nanoribbon to nanoribbon). The basis set with kinetic-energy cutoff of 400 eV has been used, and Brillouin zone have been done using a $0 \times 0 \times 0\Gamma$-centered k-point grid for the big molecular GNRs. A representative nanoribbon (the length of 2.2 nm and the width of 0.7 nm) is shown in FIG. 1, which the edges are modified with NH_2. Following the previous convention, the GNRs are defined according the number of dangling bonds on the armchair edges M and the number of dangling bonds on the zigzag edges N. The deformation are added along the zigzag edge (X direction) in the 4×9 GNRs.

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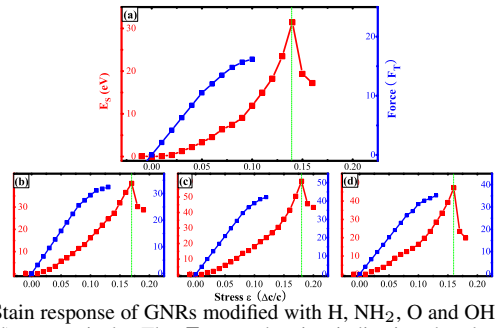

Fig. 2. Stain response of GNRs modified with H, NH_2, O and OH in (a), (b), (c) and (d), respectively; The F_T are showing indicating the elastic regime, while the E_S are showing in the whole process.

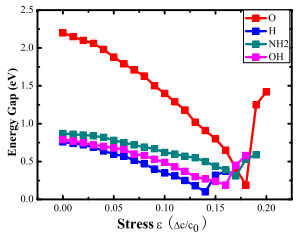

Fig. 3. The Strain-induced modulation of energy gaps of edge-modification GNRs.

III. RESULTS

All the geometric of GNRs are fully relaxed by minimizing the total energy. As a benchmark, the structures of GNRs are calculated under zero strain. The final structures of all atoms in GNRs are in a plane, and the lengths of optimized C-C bond are between 1.370Å and 1.450Å. The funny thing is that the X-axial direction bonds shorter than those other direction and the central bonds longer than the edge ones. The C-H bonds on the edges are approximately 1.090Å. The local structures of GNRs modified with O NH_2 and OH are displayed in FIG. 1. The modified angle of H-O-C is 110° and other modify angle at the zigzag are approximately 120° in GNRs. Computing by the same method, the change density analysis reveals that the total charge density inside the radius of O and N in GNRs are bigger than those in O atom and N atom. The results show that the honey structure of GNR is more likely losing electrons compared with O, NH_2 and OH.

We next investigate the mechanical properties, critical point and the energy gaps of GNRs. Elastic and plastic deformations are given along the X-axis as shown in FIG. 1. The tense forces and elastic constants are revealed form the strain energy E_S=$E_T(\varepsilon)$-$E_T(\varepsilon$=0): the total energy with the strain ε minus the total energy at zero strain (ε=$\Delta c/c_0$, c_0 being the length of GNRs at the zero strain, Δc being the length of the strain minus the length of zero strain). In this work, in order to stretch of the GNRs, we increase the optimized length in increments of $\Delta\varepsilon$=0.01 and by uniformly expanding the structure obtained from previous optimization. Then keep the left and right side fixed. Under the elastic regime, strain energy, tension force, force constant and elastic constants can be expressed as: F_T=-$\partial E_S(\epsilon)/\partial C$, C=$(1/V_0)(\partial^2 E_S/\partial\epsilon^2)$. Here V_0 is the volume of the equilibrium supercell.

The strain energy and tense force of GNRs are shown in FIG. 2. Form the result we can obtain that the covalent bond parallel to the X-axis are stretched longer than those in other direction. As a result, the elastic constants of GNRs modified with H, NH_2, O and OH are 278, 256, 354, and 293 N/m, respectively (the report experimental value for graphene is C=350±50[6]). Because of the similar honeycomb structure, their elastic constants are liking those in graphene. However, the edge effects of GNRs, their stiffness values are smaller than those of the graphene. Apparently, for the existence of double bond between C atom and O atom, the elastic constant of GNR modified with O is bigger than those in other GNRs.

This is the yielding points, where the strain energy drops suddenly. The C atom which is at the 5 site (as shown in FIG. 1) is first lose their covalent bond at the yielding points (ϵ_y) by the uniaxial tensile strain. The yielding points of elastic and plastic deformation are expecting to depend on symmetries, such as vacancy and modified. In previous reports, the ϵ_y is also depend on the temperature[7]. Just as the increase of temperature the ϵ_y is decrease. In this work, the ϵ_y of GNRs modified with H, NH_3, O and OH are 0.14, 0.17, 0.18 and 0.16, respectively. The effect of vacancy is investigated by 4×9 armchair-edge GNR modified with H. Results indicate that ϵ_y in armchair-edge is bigger than those in zigzag-edge.

Depending on their crystalline defects the energy gaps of GNRs significant variations by the uniaxial tensile strain. As strain-dependent energy gap describing in Fig. 3, we find that the energy gap decreases with the increase the strain in the elastic deformation. The energy of highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are also decrease as the increase the uniaxial strains. However, the energy of LUMO decrease speedy than those of HOMO. Energy gap increase significantly at the yielding points. Because the sp^2 C-C bond of the 5 site is broken and the modified atom (or molecule) is incorporated into the C atom. This way, be able to continuously control the band gap of modified GNRs for building the next-generation electronics.

IV. SUMMARY AND CONCLUSIONS

In conclusion, we have demonstrated that the Strain-induced modulation of mechanical properties and electronic structure of edge-modification graphene nanoribbons by first-principles calculation. We found that the final structures of all atoms in GNRs are in a plane. Furthermore, strain energy, tense force, elastic constant, critical point and energy gaps of GNRs are highly dependent on the modified atoms or molecular groups. In addition, the band gaps of GNRs can be changed significantly by the uniaxial tensile strain. The above result provide us a practical method to tune the energy gap of GNRs.

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