

Theoretical investigation on carrier mobilities of armchair graphene nanoribbons with substituted edges



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ABSTRACT

Armchair graphene nanoribbons with several substituent groups ($-\text{OH}$, $-\text{NH}_2$, $-\text{NO}_2$, $-\text{CN}$ and $-\text{Cl}$) present on the edges are investigated by using crystal orbital method based on density functional theory. It is indicated that substituting half of the edge hydrogen atoms does not significantly change the frontier band structures of the graphene nanoribbons. However, the carrier mobilities obtained from deformation potential theory are significantly modified. Activating groups especially for hydroxyl groups can greatly increase the major carrier mobilities, while deactivating groups decrease them. These can be explained by the modified frontier crystal orbitals caused by the substituent groups.

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1. Introduction

Graphene is likely to be a good carbon-based candidate for next-generation electronic devices because of its extremely high carrier mobility [1,2]. Finite width of armchair graphene nanoribbons (AGNRs) [3] can open up zero band gap of graphene [4], which is essential to give considerable on/off ratio in order to facilitate real applications. Experimentally measured carrier mobility of graphene nanoribbons at room temperature is several orders lower than that of graphene [5–8], which is caused by defects, edge roughness [6,9,10], and other structural imperfection. Fortunately, bottom-up approaches [11] based on organic synthesis give atomically precise edges of graphene nanoribbons and give an opportunity to investigate intrinsic properties of graphene nanoribbons.

Current complementary circuits in electronic industry have an advantage of low power, which require both high hole and electron mobilities of electronic devices. At room temperature, GaAs and InSb have extremely high (8000 and $80,000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) electron mobilities. However, their hole mobilities are not very high (400 and $1250 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) [12]. This is another opportunity for graphene to be a next-generation electronic device, for it has both high hole and electron mobilities [1,2]. For AGNRs, theoretical investigation indicates that both high hole and electron mobilities should be achieved depending on the width of the nanoribbons [13].

For large scale industrial application, a small improvement should give huge benefits. Carbon nanotube computer has already arrived [14]. It is urgent and essential to explore the possibility of enhancing the carrier mobilities of graphene nanoribbons, before it

comes into real manufacture. A graphene nanoribbon has honeycomb structure and can be viewed as a large aromatic system. It is well known that a typical aromatic system is a benzene molecule. A substituent effect is a common property of benzene molecules and significantly affects their properties. A benzene molecule can be activated or deactivated depending on the types of the substituent groups. Similarly, substituted graphene nanoribbons should also have properties different from perfect graphene nanoribbons. The aim of this work is to find out *whether carrier mobilities of substituted AGNRs can be higher than those of the perfect ones?* In the present work, graphene nanoribbons with edge hydrogens (exist in the synthesized graphene nanoribbons [11]) substituted by activating or deactivating groups are investigated by using crystal orbital method based on density functional theory. Carrier mobilities of these structures are analyzed under deformation potential theory.

2. Models and computational details

Two activating groups ($-\text{OH}$ and $-\text{NH}_2$) and three deactivating groups ($-\text{NO}_2$, $-\text{CN}$ and $-\text{Cl}$) are considered to investigate the substituent effects. As shown in Fig. 1, if all the four edge hydrogens (H_1 , H_2 , H_3 and H_4) are substituted by the substituent groups, the atoms at the edges are crowded and will result in rippled edges [15–17]. This should perturb the conjugated structures of graphene nanoribbons and is not beneficial to the carrier mobilities, so all hydrogen-substitution is not investigated here. Considering that substituting of H_1 and H_3 at only one edge in Fig. 1 should be very challenging to experiments, two edges should be substituted meantime. Structures with H_1 and H_2 substituted or H_1 and H_4

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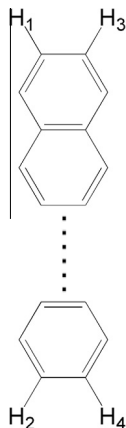


Fig. 1. Models of AGNR-X.

substituted are two substituted derivatives considered here (denoted as N -AGNR-X, where N is the number of carbon atoms perpendicular to the extended direction, $N = 10$ –31).

The substituted derivatives of AGNRs are fully optimized by using crystal orbital method with CRYSTAL06 program [18]. Hybrid density functional B3LYP(VWN5) [19,20] as well as Bloch functions constructed with 6-21G(d, p) basis set are used in the calculations. Default convergence criteria in the program are used. A Monkhorst–Pack sampling with 41 k -points in the first Brillouin zone is adopted in the self-consistent iteration procedure and the k -points net is sufficient to obtain converged energy and related electronic properties. A uniform k -points sampling with 800 points is adopted in the non-iterative band structure calculation in order to fit of the parameters needed for carrier mobility calculations.

Under deformation potential theory, electron wavelength is assumed to be comparable to acoustic phonon's, so carriers are mostly scattered by acoustic phonons [21]. For one-dimensional structures, carrier mobilities are obtained by

$$\mu = \frac{eh^2C}{(2\pi k_B T)^{1/2} |m^*|^{3/2} E_1^2}, \quad (1)$$

where parameter stretching modulus C and deformation potential constant E_1 are obtained under deformed geometries according to longitudinal acoustic phonon along one-dimensional direction [22], carrier effective mass m^* is calculated by fitting frontier bands. It is noted that when carrier density of state does not have a very sharp shape near edge of frontier bands, carriers in an energy range wider than thermal energy $k_B T$ could also contribute to real conduction process. In this work, $10k_B T$ as suggested [23] is used to fit the carrier effective mass and then to obtain the carrier mobility. It should be noted that the scattering mechanism for carrier transport in graphene still remains unclear. However, the carrier mobility of graphene calculated under deformation potential theory [24] agrees well with the experimental result [25]. The deformation potential approach has also been successfully applied to carbon nanotubes [26–28], graphene nanoribbons [13,29,30] and silicene nanoribbons [31]. From the deformation potential theory, it is indicated that high mechanical properties, low deformation potentials and small carrier masses are favorable to high carrier mobilities.

3. Results and discussion

3.1. Structures and stabilities

The structural optimization of the N -AGNR-X ($N = 10$ –31) indicates that the substitution only slightly modifies the carbon

networks. For example, the C–C bonds in the middle are around 0.143 nm, which are slightly longer than those of the N -AGNR-H (0.142 nm). The C–C bonds at the edges are in the range of 0.136–0.137 nm, which are slightly shorter than those of the N -AGNR-H (0.137 nm). The substitution does not change the basic plane of the graphene nanoribbons and all the carbon atoms are in the same plane. For –OH, –CN and –Cl substitution, the substituent groups are also in the same plane of the carbon networks. For –NH₂ and –NO₂ groups with three atoms, the nitrogen atoms derive slightly from the plane to make groups far away from the hydrogen atoms on the adjacent carbon atoms. This is the main character of the substituted derivatives. The derivations of nitrogen atoms are less than 10° and 20° for –NH₂ and –NO₂ groups, respectively.

The energy differences are quite small for the two models with H₁ and H₂ substituted or H₁ and H₄ substituted in Fig. 1. For example, the energy of 10-AGNR-OH with H₁ and H₄ substituted by two hydroxyl groups is 0.01 eV (only 0.0004 eV per atom) lower than that of the model with H₁ and H₂ substituted. It is noted that the band structures described below are similar for the two models, and the band-structure-derived properties also have no essential difference. For the sake of brevity, the following discussions are all based on the model with H₁ and H₄ substituted.

In order to investigate the stabilities of the AGNR-X, edge formation energies [32] with respect to parent graphene are calculated. For example, the edge formation energy of AGNR-OH is defined as

$$\frac{1}{2L} \left(E_{\text{AGNR-OH}} - \frac{N_C}{2} E_{\text{graphene}} - \frac{N_H}{2} E_{\text{H}_2} - \frac{N_O}{2} E_{\text{O}_2} \right), \quad (2)$$

where L is the cell parameter, N_C , N_H and N_O are the numbers of carbon, hydrogen and oxygen atoms in AGNR-OH, respectively. The edge formation energies of AGNR-OH are from –0.364 to –0.352 eV Å^{–1}. For –NH₂, –NO₂, –CN and –Cl substitutions, the edge formation energies are in the range of 0.052–0.065, 0.129–0.142, 0.387–0.398 and 0.086–0.094 eV Å^{–1}, respectively. The edge formation energy reflects the energy change per edge length from the parent graphene and the elementary substances to the substituted derivative. It is indicated that the formation of AGNR-OH is energetically favorable, while it is endothermic for other structures. However, the edge formation energies for –NH₂ and –Cl substitutions are near zero. Although the –CN substitution is quite endothermic, it may be synthesized through multi-step reactions, such as diazotization. It is beneficial to explore their properties before they are synthesized.

The structures 10-AGNR-X ($X = \text{–OH, NH}_2, \text{NO}_2, \text{CN}$ and Cl) are also investigated with spin-polarized calculations by using VASP program [33]. Both PBE functional [34] and B3LYP hybrid functional in combination with PAW potential [35] are adopted. No spin polarization is found in these structures, so all the discussions in this work are based on close-shell results.

3.2. Band gaps

Direct band gaps exist at the center of the first Brillouin zone for all the AGNR-X. As an example, the band structures of 15-AGNR-OH are shown in Fig. 2(a). Compared with AGNR-H [30], the changes of the frontier band structures as well as the band gaps are small. The reason is that the frontier crystal orbitals of AGNR-H are distributed on all the carbon atoms, so only edge substitution should not significantly modify the frontier band structures. This gives the possibility of maintaining the basic properties of AGNR-H derived from the frontier bands, such as high carrier mobilities.

The band gaps of AGNR-X oscillate with the width N . The band gap sequence of AGNR-NO₂ or AGNR-CN are $\text{gap}_{3q+1} > \text{gap}_{3q}$ –

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