Tuning the electronic structure of graphene nanoribbons through chemical edge modification: A theoretical study

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We report combined first-principle and tight-binding (TB) calculations to simulate the effects of chemical edge modifications on structural and electronic properties. The C-C bond lengths and bond angles near the graphene nanoribbon (GNR) edge have considerable changes when edge carbon atoms are bounded to different atoms. By introducing a phenomenological hopping parameter t_1 for nearest-neighbor hopping to represent various chemical edge modifications, we investigated the electronic structural changes of nanoribbons with different widths based on the tight-binding scheme. Theoretical results show that addends can change the band structures of armchair GNRs and even result in observable metal-to-insulator transition.

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Carbon nanotubes (CNTs) with chiral vectors (n,m) are metallic when $(2n+m)$ or equivalently $(n-m)$ is a multiple of 3. Armchair CNTs with chiral vectors (n,n) are always metallic while the zigzag CNTs $(n,0)$ are metallic only when n is a multiple of 3. In general, the electronic properties can be modified by attaching atoms or molecules along CNTs' sidewalls using chemical methods.[1–3] The recent development of graphene, a sheet of an unrolled CNT, has attracted a great deal of research attention.[4,5] Graphene is a two-dimensional one-atom-thick carbon layer with carbon atoms arranged in a honeycomb lattice. Experiments by using the mechanical method and the epitaxial growth method show it is possible to make graphene nanoribbons (GNRs) with various widths.[5–7] Several experiments have also been performed recently to investigate the transport properties of graphene.[5] The results show that graphene is an interesting conductor in which electrons move like massless and relativistic particles. Several groups show STM/STS graphene images with well-defined hydrogen-terminated edges in an ultrahigh-vacuum (UHV) environment.[8–10]

An interesting question to investigate is whether a metallic CNT is still metallic when it is unwrapped into a graphene nanoribbon (GNR).[11–13] For simplicity, we choose the same definition for GNRs as for CNTs in this paper. An unwrapped (n,m) CNT, for instance, is called a (n,m) GNR. Previous theoretical studies based on the tight-binding (TB) approximation have examined the electronic states and energy dispersion relations of GNRs with the assumption that hydrogen atoms are attached to the carbon atoms on the GNR edge. These calculations show that the metallic or insulating feature in GNRs are different from that in CNTs.[14–16] Zigzag GNRs (n,n), which correspond to unwrapped armchair CNTs with zigzag edges, are still metallic (if the spin degree of freedom is not considered). The electronic structure of armchair $(n,0)$ GNRs depends strongly on the nanoribbon width.[14–16] Armchair GNRs are metallic when $n=3p+1$ (p is an integer), and otherwise they are insulating. That is to say, GNRs can be made either as metallic or as semiconducting materials by controlling their width or

chirality. This remarkable characteristic is very useful in making graphene-based nanoscale devices. In addition, GNRs are much easier to manipulate than CNTs due to their flat structure, and thus they can be tailored by using lithography and etching techniques.

Because each edge carbon atom of GNRs is only bounded to two neighboring carbon atoms, a dangling carbon bond offers a remarkable opportunity to manipulate the electronic properties of GNRs. This can be done by attaching different atoms or functional molecular groups to the dangling carbon atom. Similar to the functionalization of CNT devices along edge dangling bonds,[2,3,17] the electronic properties of GNRs can also be alternated by chemical edge modifications. In this paper, we examine the geometric deformation of finite-width armchair GNRs caused by different edge addends. Our first-principle calculations show that the C-C bond length and bond angle near the edge undergo observable changes. To include the effect of the deformation on the graphene ribbon edge, we introduce a phenomenological hopping parameter t_1 in our TB approximation calculations. Our simulations show that the energy gap depends on ribbon width and hopping parameter t_1. A nonzero energy gap exists for $(3p+1,0)$ armchair GNRs, which means the metal-to-insulator transition can be achieved by edge modifications.

The increments of C-C bonds and bonding angles at the nanoribbon edge have been reported based on the TB approximation calculations.[11–13] In this paper, we first estimate nanoribbon geometric deformation caused by various chemical addends. For a simple case (each armchair GNR edge carbon atom is saturated by one hydrogen atom), we evaluate geometric and electronic structure changes using the first-principle method. Our optimizations employ the Vienna *ab initio* simulation package,[18,19] which is implemented based on the local density approximation[20] of the density-functional theory (DFT).[21] The electron-ion interaction is described by the ultrasoft pseudopotentials[22] and the energy cutoff is set to be 286.6 eV. The atoms' positions are optimized in order to reach the minimum energy with the Hellmann-Feynman forces less than 0.02 eV/Å. The results
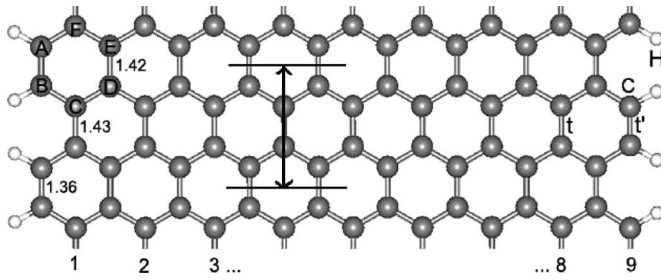
FIG. 1. Optimized structure of a (9,0) armchair GNR (all edge bonds are bound by hydrogen atoms). Here, the bond length is in Å. Note that a zigzag $(n,0)$ GNR can be rolled to form an armchair $[(n,0)$ CNT, and an armchair (n,n) GNR can be rolled as a zigzag $(n,n)]$ CNT.

show that the geometric relaxation localizes near the edge. Only the bond lengths and angles of edge carbon atoms in armchair GNRs have considerable changes comparing with those of ideal graphene ribbons. For example, $\angle BAF = 121.6°$ and $\angle BCD = 118.3°$. The interatomic distance between A and B sites (d_{AB}) of (9,0) GNR is reduced from 1.42 Å to 1.36 Å, and $d_{BC} = 1.40$ Å $d_{CD} = 1.40$ Å and $d_{DE} = 1.42$ Å, respectively, as shown in Fig. 1.

The geometric deformation of armchair GNRs, however, depends on various kinds of chemical addends. For example, the edge carbon atoms connect to F atoms, the edge C-C bond lengths shorten to be 1.35 Å (decreasing about 5%). In general, this kind of geometric deformation results in the changes of hopping parameter between two neighboring carbon atoms on the GNR edge. The parameter change is defined as

$$\Delta t = \frac{\langle 2p_z'|\hat{H}_1|2p_z'\rangle - \langle 2p_z|\hat{H}_0|2p_z\rangle}{\langle 2p_z|\hat{H}_0|2p_z\rangle}. \quad (1)$$

Here, $\hat{H}_1$ and $\hat{H}_0$ are the Hamiltonians of the system with and without chemical edge modification, respectively. $2p_z'$ and $2p_z$ are the atomic orbitals of the coupled neighboring carbon atoms at the edge with the optimized bond length and with the bond length of 1.42 Å, respectively. Our calculations are conducted by using the SIESTA code in real space and single-zeta (SZ) basis.[23] One can expect that the edge hopping parameter can increase (or decrease) as edge C-C distance is shortened (or expanded). The edge hopping parameter change for the hydrogen-saturated case is predicted to be 10.1% based on the DFT, which is consistent with the numerical result based on the TB approximation.[24]

In previous TB approximation calculations,[12,25] the dangling bonds are assumed to be saturated by hydrogen atoms and thus all transfer integrals between the nearest-neighbor sites are set to have the same values. This simple choice of hopping parameter, however, does not consider geometric distortions at the nanoribbon edge. It is important to extend this existing scheme in order to understand the impacts of chemical edge modification on electronic properties of armchair GNRs. For simplicity, we adopt the TB approach to study these impacts. We choose the value of t_1 either smaller or larger than the hopping parameter $t = 2.66$ eV of inner C-C
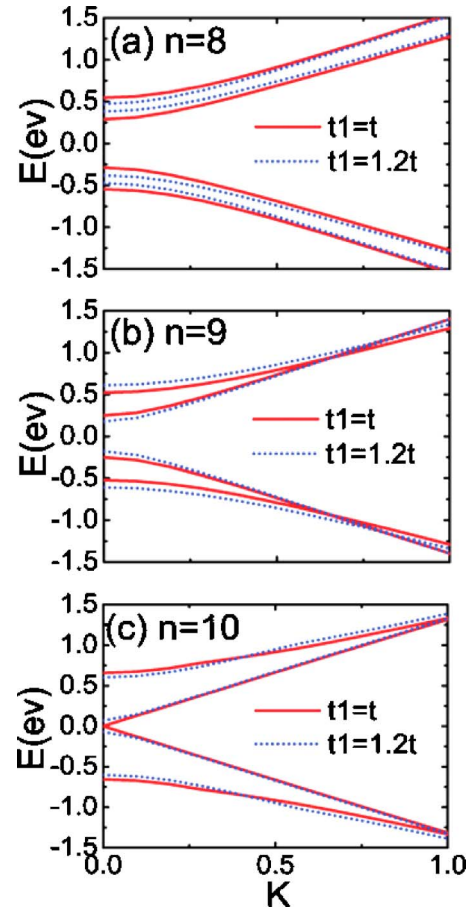

FIG. 2. (Color online) Top two valence bands and bottom two conduction bands of zigzag GNRs in $t_1 = t$ and $t_1 = 1.2t$ cases. Here $t = -2.66$ eV is the hopping parameter of two-dimensional infinite graphene with the lattice constant $a_{c-c} = 1.42$ Å.

bonds to simulate different chemical addends. Our theoretical results show that only parameter t_1 is sufficient to describe the electronic structure changes of armchair GNRs.

Next, we calculate the band structures of armchair GNRs, when edge GNR dangling bonds are bounded by atoms or molecular groups. We select ideal armchair GNRs with indices $(n,0)$ and calculate the band structures of three different ribbon widths ($n = 8, 9$, and 10) by setting $t_1 = t$. The results are shown in Figs. 2(a)–2(c) for $n = 8, 9$, and 10 with red solid lines, respectively. For clarity, we set the Fermi level to zero ($E_F = 0$) and the wave number is normalized by the primitive translation vector for each GNR. In this study, we choose (8,0), (9,0), and (10,0) GNRs (their widths are around 2 nm) as examples to represent $(3p+2,0)$, $(3p,0)$, and $(3p+1,0)$ GNRs (where p is an integer; and they correspond to three different width armchair GNRs labeled with $(3p+1,0)$, $(3p,0)$, and $(3p+2,0)$ in the literature[26]). It is clear that the band structure of an armchair GNR depends on its width, and the energy gap is 0.58, 0.50, and 0.0 eV for (8,0), (9,0), and (10,0) armchair GNRs, respectively. Armchair GNRs $(n,0)$ are metallic when $n = 3p+1$ as shown in Fig. 2(c). The energy gaps are nonzero for $n = 3p$ and $n = 3p+2$ GNR, in which GNRs become insulating. This result matches the previous reported results.[12] To simulate chemi-
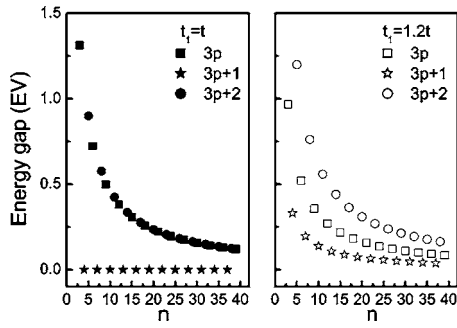
FIG. 3. The energy gap of armchair GNRs depends on their widths: (a) when $t_1=t$ and (b) when $t_1=1.2t$.

FIG. 4. (Color online) The effect of hopping parameter t_1 on energy gaps of armchair GNRs with different widths ($n=8$, 9, and 10).

cal edge modification effects, t_1 is set to be $1.2t$. The π and $\pi^\star$ conduction bands are no longer degenerate at $k=0$ for a (10,0) GNR and energy gap becomes 0.14 eV, which leads to metal-to-insulator transition. The DFT results suggest that both quantum confinement and edge effect cause the opening of energy gap.[26] Although (8,0) and (9,0) GNRs remain insulating when $t_1=1.2t$, the energy gap is changed to 0.76 eV (increased) and 0.36 eV (decreased) by changing of the edge hopping parameter. Obviously, these theoretical results show that the electronic property of armchair GNRs is tunable via chemical edge modification.

The band structure of zigzag (n,n) GNRs are similar to those of CNTs except for the existence of edge states that are caused by the gauge field at GNR edges.[12,13] Due to the localized states at the edges, the uppermost valence band and the lowest conduction band are always degenerated at the Fermi level when $k_0 \leq |k| \leq \pi$. k_0 is slightly less than $2\pi/3$ for finite-width zigzag GNRs. If considering the spin degree of freedom in the DFT calculations, a hydrogen-saturated zigzag GNR is predicted to have a magnetic insulating ground state.[26] By selecting different t_1, we observe that the electronic structure near the Fermi level changes slightly, which indicates the electronic properties or carrier transport of zigzag GNRs are stable and insensitive to the edge modifications.

Figure 3 shows the relationship between armchair GNR widths (n) and their energy gaps when choosing $t_1=t$ and $t_1=1.2t$. For $n=3p$, the energy gap of $t_1=1.2t$ is smaller than that of $t_1=t$. This value decreases when the width increases. For $n=3p+1$, the energy gap of $t_1=t$ is zero, which becomes independent of ribbon width n. For $t_1=1.2t$, C-C bonds on the edge are shortened and the energy gap opens in $(3p+1,0)$ armchair GNRs. For $n=3p+2$, the energy gaps of $t_1=t$ are nearly the same as that of $t_1=1.2t$. By comparing the electronic structure of $t_1=t$ with those of $t_1=1.2t$, we observe that the change of the edge hopping parameter (resulting from the added chemical groups) can significantly affect the electronic properties of armchair GNRs. Our calculations reproduce the results based on the local density approximation of the DFT.[26] It is worth mentioning that the energy gaps of both $t_1=t$ and $t_1=1.2t$ approach zero, or the effect resulting from the addends becomes insignificant when n is very large. This observation suggests that tuning band structure through edge modifications is effective only for finite-width GNR.
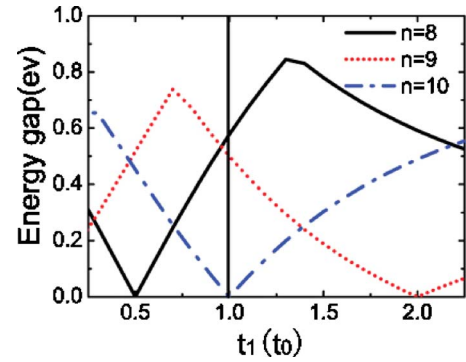
Next, we focus on evaluating the energy gap as a function of hopping parameter t_1 for three kinds of armchair GNRs [(8,0), (9,0), and (10,0)]. Results are plotted in Fig. 4. It is interesting to note that around $t_1=t$ (representing the slight deformation case), the energy gaps of (8,0), (9,0), and (10,0) armchair GNRs show different trends. In contrast to a (9,0) GNR, the energy gap of a (8,0) GNR increases as t_1 increases around $t_1=t$. This trend is also appreciable in Fig. 2. A (10,0) GNR has a zero energy gap at $t_1=t$.[11–13] Once we applied chemical edge modifications $(t_1 \neq t)$, there is an opened energy gap that always increases no matter whether t_1 decreases $(t_1 \leq t)$ or increases $(t_1 \geq t)$. This result shows that a transition between metallic and insulating GNRs is achievable. Moreover, the energy gap can be controlled by selecting proper addends bounded to the edge carbon atoms of armchair GNRs.

In Fig. 4, one t_1 value exists that corresponds to the zero energy gap for both (8,0) and (9,0) armchair GNRs. This phenomenon shows that, in principle, insulating armchair GNRs can be modified and become metallic GNRs. However, this kind of modification is difficult to implement since the hopping parameter t_1 would have to be reduced or enlarged by 100%.

In conclusion, first-principles calculations show that the chemical modification of armchair GNRs results in a considerable deformation of the bond lengths and bond angles near the edge. The introduction of hopping parameter, t_1, in the TB scheme accurately capture the effects caused by chemical edge modifications. Our theoretical results show that addends can change armchair GNRs' band structures and even lead to observable metal-to-insulator transitions. It should be pointed out that the chemical edge modification is effective only for finite-width GNRs.

Note. After submitting this paper, we became aware of the similar independent work conducted by Son, Cohen, and Louie *et al.*[26] In their paper,[26] the scaling rules for GNR band gap as a function of their widths and their origins are studied based on the first-principles approach. A lattice model is then adopted within TB approximation to explain the changes of energy gap in armchair GNRs by resolving the Hamiltonian perturbatively. Our numerical results presented in this paper are obtained by using the exact diagonalization technique.

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