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Communication

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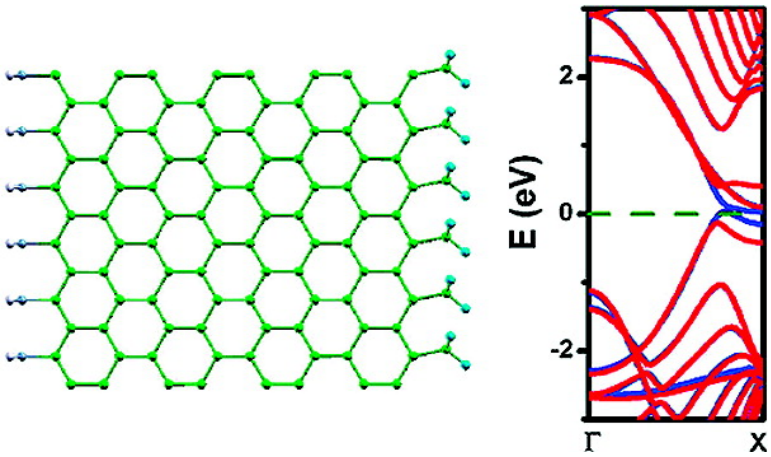

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Half-Metallicity in Edge-Modified Zigzag Graphene Nanoribbons

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After its successful experimental realization,[1] graphene nanoribbon (GNR) becomes an important candidate for future nanoelectronics.[2−5] Similar to carbon nanotube (CNT), it has a one-dimensional structure with hexagonal two-dimensional carbon lattice. However, it is easier to make microscale devices from planar GNR than from CNT, by using, for example, the standard lithographic techniques.[1,3,4] Both the magnetic properties[6−9] of GNR and its band gap engineering[10−14] have been extensively studied, and the reduced dimension of the ribbon introduces important edge effects.[15−17] It is now well-known that zigzag edge GNR (ZGNR) is a semiconductor with two electronic edge states,[10,18,19] which are ferromagnetically ordered but antiferromagnetically coupled to each other. Based on a theoretical investigation, Son et al.[20] predicted that ZGNR becomes half-metallic when an external transverse electric field is applied. This result opens the possibility of spintronics application for graphene. Our recent calculations confirmed their prediction[21] and demonstrated that a very high critical electric field is required to achieve half-metallicity, which suggests that the realization of half-metallicity is practically difficult.

Chemical decoration is an alternative way to convert ZGNR to half metal. Effects of edge modification on the ZGNR electronic structure have been studied previously.[22,23] The carbon π orbitals at the edges were found to shift under effective potential induced by functional groups, which suggests that ZGNRs may become spin-selective materials by edge modification. As shown in Figure 1a, when the ZGNR is terminated by the same groups (H in the figure) at both edges, the two edge states are degenerated in energy. One state occupied by spin-down electrons, and the other occupied by spin-up electrons. When the two edges are modified with different groups, the corresponding potential shifts are different. The system then becomes spin selective as illustrated in Figure 1b. Once the potential difference is large enough, conduction band (CB) and valence band (VB) in one spin channel (spin-down channel in Figure 1) will overlap in energy, and the ZGNR is expected to become half metal.

In this communication, we examine the proposal to realize half-metallicity in ZGNRs by edge modification. First-principles calculations have been performed. For more computational details, please refer to the Supporting Information. We consider the following functional groups: H, NH_2, NO_2, and CH_3. Since different effective potentials at the two edges are desirable, a donor and an acceptor group should be a good chemical modification pair. As shown in Figure 2a, NH_2 and NO_2 are added to the two edges of the ZGNR with 8-zigzag chains (8-ZGNR). Both NH_2 and NO_2 groups compensate the dangling sp^2 σ orbitals at edge carbon atoms, leading to the in-plane σ and σ^* bands removed from the vicinity of the Fermi level. The edge states close to the X point show a metallic spin-down channel and a semiconductor spin-up channel,

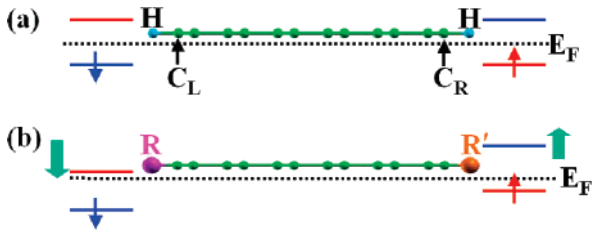

Figure 1. (a) Structures of the H-saturated ZGNR and schematic energy diagram for the edge states. Green and sapphire balls denote carbon and hydrogen atoms, respectively. (b) Schematic edge-state energy diagram of ZGNR with different chemical modifications at the two edges. R (magenta) and R′ (orange) represent different functional groups. Red energy levels for the spin-up channel, and blue for the spin-down channel.

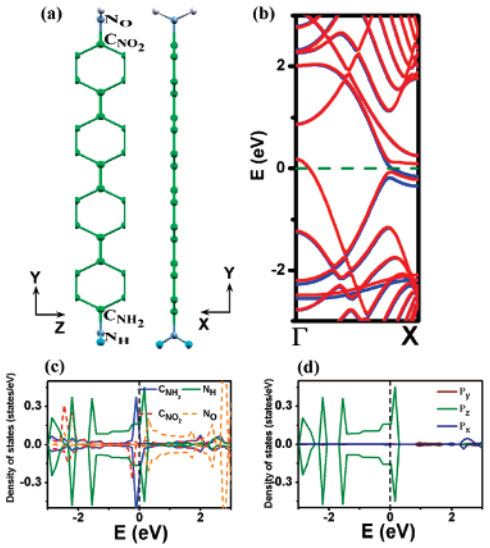

Figure 2. (a) Structures of 8-ZGNR with NH_2 at one edge, and NO_2 on the other side. Left: top view. Right: side view. Green, white, gray, and sapphire balls denote carbon, oxygen, nitrogen, and hydrogen atoms, respectively. (b) Its band structure. Red lines are in the spin-up channel, and blue lines represent the spin-down channel. (c) Its projected density of states (PDOS). (d) PDOS of nitrogen atoms in the NH_2 groups.

as we expected. However, close to the Γ point, there is a spin unpolarized band across the Fermi level, which makes both spin channels metallic. The projected density of states (PDOS) analysis reveals that this band is mainly contributed by the p_z orbitals of NH_2 groups. Therefore, the N lone pair electrons in NH_2 are responsible for the metallicity in the spin-up channel.

To exclude the effect of the NH_2 lone pair electrons at the Fermi level, we have tried to substitute the NH_2 groups with H atoms and CH_3 groups. However, as shown in Figure S1, 8-ZGNRs with the NO_2-H pair are semiconducting. In Figure 3a, the band structure of 8-ZGNRs with the NO_2-CH_3 pair is plotted, and a half-metallic property is observed. Energy gap in the spin-down channel closes

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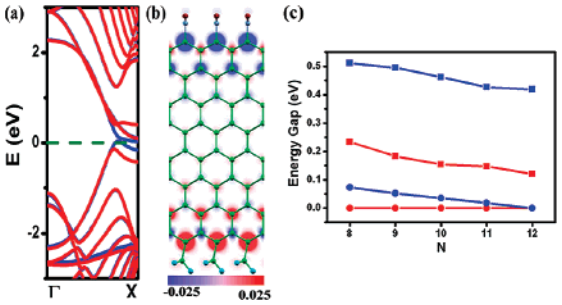

Figure 3. (a) Band structure and (b) spin density of ZGNRs modified by the NO_2-CH_3 pair. Red represents the spin-up channel, and blue represents the spin-down channel. (c) The band gaps of ZGNR-full (red) and ZGNR-half (blue) with spin-up (squre) and spin-down (circle) channels. Please refer to the text for the definitions of ZGNR-full and ZGNR-half.

around the X point, just as in the NO_2-NH_2 pair. The spin density for the ZGNR with the NO_2-CH_3 pair (Figure 3b) mainly distributes on the edge atoms. This is because that, as in H termination, the NO_2 and CH_3 groups compensate the dangling sp^2 σ orbitals at each carbon edge site and have little contribution to the π orbitals of the edge states. However, the higher electron density will lift the energy of occupied orbitals. The band gaps of the ZGNRs are thus reduced, as shown in previous results.[22,23]

The relative stability of edge-modified ZGNRs is very important in practice. Because these structures have different chemical compositions, the binding energy per atom does not provide a suitable measurement for the comparison of their relative stability. Therefore, we adopt the approach used in tertiary phase thermodynamics to account for chemical composition and to analyze the relative stability of functional ZGNRs.[22] We define a Gibbs free energy of formation δG for edge-modified ZGNRs as $\delta G = E_c - n_H\mu_H - n_O\mu_O - n_N\mu_N - n_C\mu_C$, where E_c is the cohesive energy per atom of chemically functionalized ZGNRs, and n_i is the molar fraction of atom i (i = C, O, H, N) in the ribbons, satisfying the relation $n_H + n_O + n_N + n_C = 1$. The binding energy per atom of H_2, N_2, and O_2 molecules are chosen as μ_H, μ_O, and μ_N, respectively, and μ_C is the cohesive energy per atom of the infinite graphene. ZGNR modified by one NO_2-CH_3 pair per ZGNR unit (ZGNR-full) is less stable and has a larger δG than the H-saturated one. This is easy to understand since the nearest-neighboring NO_2 and CH_3 group repulsion is too large at short distances. To obtain more stable products, we construct a new structure, where there is only one NO_2 and CH_3 pair every two unit cells (ZGNR-half). Because the distances between the neighboring CH_3 groups are larger than 4.5 Å now, the calculated Gibbs free energy of formation is greatly reduced. ZGNR-half is even more stable than H-saturated ZGNR.

As shown in Figure 3c, ZGNR-half becomes a spin selective semiconductor, but we find that the spin-down gap becomes narrower when the ribbon width increases. ZGNR-half turns to half metal when it is wider than 12-zigzag chains. We also checked the ribbon width dependence for ZGNR-full. At high NO_2 and CH_3 concentration, the nanoribbon is always half metal for a width larger than 8. Therefore, the only difference brought by the terminal group concentration is the critical width to obtain half-metallicity, which is because of the difference of the effective potential shift at the edges. In our ZGNR-half structure, the NO_2-CH_3 pair is located on the same armchair C atom row. We have also tested the condition where the NO_2 and CH_3 groups are at different C atom rows and have found no qualitative difference. We also expect to get half metals with lower terminal group concentrations in wider nanoribbons. It is also interesting to note that different types of spin-down band gap are observed. It is direct for ZGNR-full and indirect for ZGNR-half (Figure S3). Such a difference is expected to be important for the optical property of ZGNRs.

In summary, we have presented a detailed study on the electronic properties and relative stabilities of several edge-modified ZGNRs. Some wide ribbons with NO_2 groups at one edge and CH_3 groups at the other edge are half metal. By reducing the concentration of big functional groups, the half-metallic ribbons can be more stable than H-saturated ones. Our results thus provide a practical way to produce ZGNR based spintronic devices.

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Supporting Information Available: Computational details, band structures of other calculated ZGNR models, and free energy of formation for ZGNR-full and ZGNR-half with different widths. This material is available free of charge via the Internet at http://pubs.acs.org.

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