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Materials design of half-metallic graphene and graphene nanoribbons

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Through patterned chemical modification, we show that both graphene sheets and zigzag-edged graphene nanoribbons (ZGNRs) can be converted to half-metals as long as the unmodified carbon strip (or width of ZGNRs) is sufficiently wide. Periodically functionalized graphene can mimic electronic behavior of edge-modified ZGNRs as the edge-modified zigzag carbon chains effectively divide a graphene sheet into a series of identical ZGNRs. © 2009 American Institute of Physics. [DOI: 10.1063/1.3143611]

Graphene, the thinnest freestanding material revealed to date, has attracted enormous interest owing to its potentially tunable electronic properties.^{1–4} Pristine graphene is a zero-bandgap semimetal and is chemically inert. A recent experimental breakthrough demonstrated that a graphene can be chemically converted into graphane through hydrogenation (by reacting with atomic hydrogen),⁵ which transforms the semimetal into an insulator.^{6,7} In addition, functionalized single graphene sheets (FSGs) have been fabricated via partial reduction of graphite oxide.⁸ The latter is graphene densely covered with hydroxyl and epoxide groups.^{9,10} *Ab initio* calculations suggest that FSGs might be wide graphene nanoribbons (GNRs) with epoxy groups chemisorbed in the middle.⁸

A GNR is known to be a semiconductor,¹¹ but a zigzag-edged GNR (ZGNR) can be transformed into a half-metal either by applying an in-plane electric field^{11,12} or through chemical modification of the edges with different functional groups.^{12–17} In this letter, we show that a graphene sheet can be also converted into a half-metal through patterned chemical modification (e.g., fluorination and hydroxylation) of selected periodic carbon chains, mimicking edge modification of ZGNRs. A known strategy to achieve half-metallicity in ZGNRs is to create large potential difference between the two edges through chemical modification of one edge with electron donating groups while another edge with electron accepting groups.¹⁵ We show that on a graphene, periodically modified strips of carbon chains can be viewed as boundaries that effectively divide the graphene into identical “nanoribbons” thereby leading to spin state similar to the edge state of ZGNRs.¹⁸

As a proof of principle, we first present a computer-aided material design of edge modification to achieve half-metallicity in ZGNRs. A previous study has shown that multiatom functional groups such as NO₂ and CH₃ can be used for chemically modifying edges of ZGNRs to achieve half-metallicity.^{12,13,15} However, the large steric interaction between neighbor groups prevent them to be effective for chemical modification of neighboring carbon chains on a graphene sheet. Hence, our design mainly utilizes single-atom and two-atom functional groups for the chemical modification.^{14,16,17}

To assess effect of the chemical modification on electronic properties of ZGNRs (and graphene), we performed spin-polarized density functional theory (DFT) calculation using DMOL3 program package¹⁹ (see supplemental

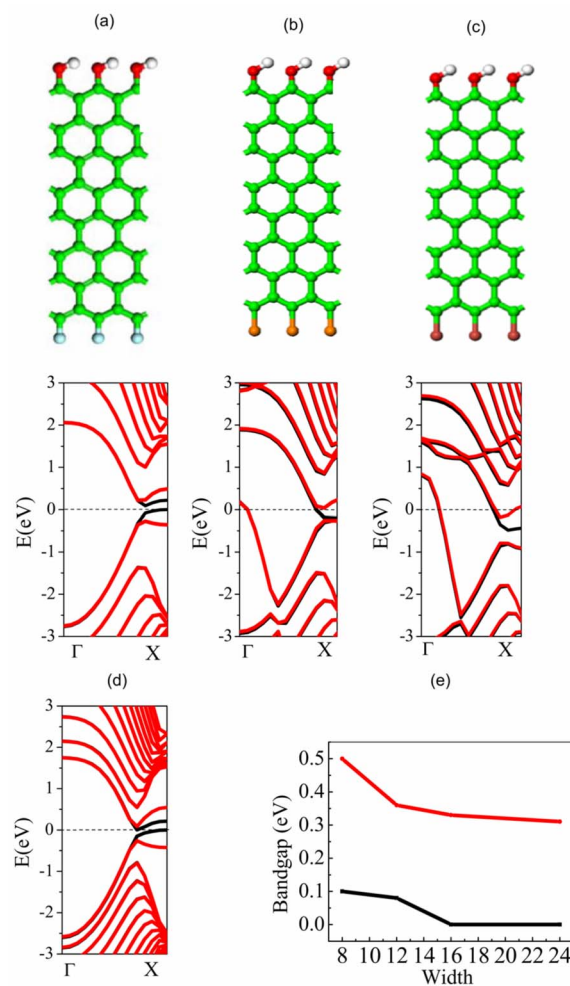


FIG. 1. (Color online) Geometric structure and electronic band structure of an 8-ZGNR with two edges chemically modified by OH and (a) F, (b) Cl, and (c) Br, respectively. The green, red, blue, orange, red-brown and white spheres denote C, O, F, Cl, Br, and H atoms, respectively. (d) Electronic band structure of 16-ZGNR modified by OH and F. (e) Spin-resolved band gap versus the width of ZGNR. Red and black lines denote α and β spin channel, respectively.

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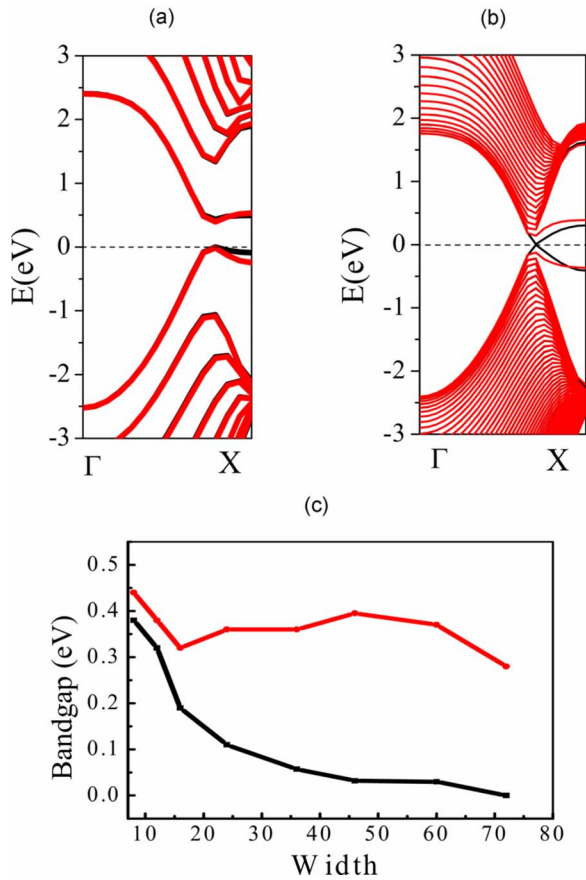


FIG. 2. (Color online) Electronic band structures of (a) 8-ZGNR and (b) 72-ZGNR, with two edges modified by H and F, respectively. (c) Spin-resolved band gap versus the width of ZGNR. Red and black lines denote α and β spin channel, respectively.

materials²⁰). We examined a number of functional groups and found that the OH group is an effective electron-donating group for chemical modification of one edge, and F atom is an effective electron-accepting group for chemical modification of the other. Hereafter, we label a GNR with n zigzag chains as n -ZGNR. Figures 1(a)–1(c) show the chemically modified 8-ZGNRs with one edge fully modified by OH groups and another by F, Cl, or Br atoms, and their calculated spin-resolved electronic band structures. It is revealed that only edge modification by F atoms leads to a semiconducting spin channel while others all lead to metallic channels.

As the width of F -modified ZGNR is prolonged to 16, as shown in Fig. 1(d) and Fig. S1 (see supplemental materials²⁰), its electronic band structure and density of states (DOS) indicate that the chemically modified ZGNR becomes a half-metal. Dependence of the spin-resolved band gap on the width of ZGNRs is shown in Fig. 1(e). Here, the gap-opening channel is designated as α spin channel and the gap-narrowing channel is designated as the β spin channel. As the width of ZGNRs increases, bandgaps of both spin channels are reduced, and the band gap of the β spin channel is closed at $n=16$. In the latter case, the potential difference due to the edge modification is sufficiently large to push the edge state to the Fermi level, resulting in half-metallicity. Figure 1(e) shows that narrow-width edge-modified ZGNRs ($n < 16$) are typically spin-polarized semiconductors whereas wide-width ZGNRs ($n > 16$) are half-metals.

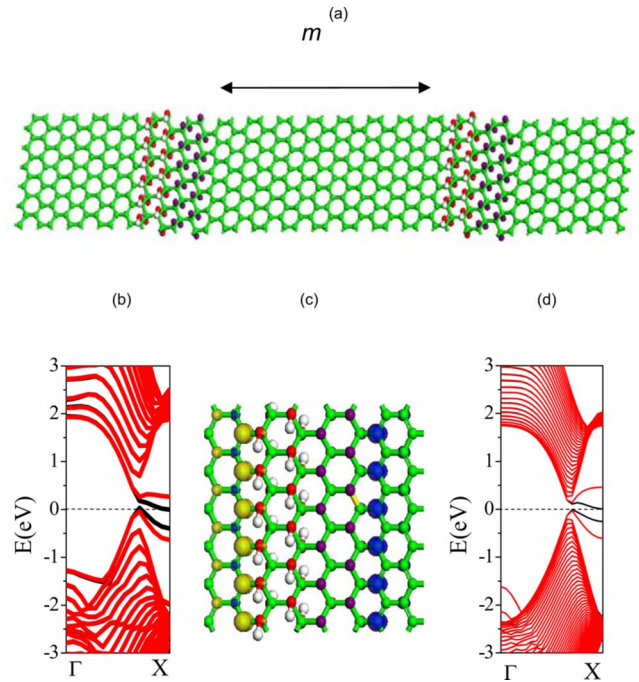


FIG. 3. (Color online) (a) Geometric Structure, (b) electronic band structure and (c) spin density distribution of chemically modified graphene, where two neighboring zigzag carbon chains are modified by OH groups and the two chains next to them are modified by F atoms. The unmodified strip has $m=16$ zigzag carbon chains. Green, red, purple and white spheres denote C, O, F, and H atoms, respectively. Blue and yellow represent isosurface of α and β spin density, respectively. The range of isovalues for spin density is within $[-0.03, 0.03]$. (d) Electronic band structure of graphene chemically modified with two chains of H and two chains of F. The unmodified strip has $m=72$ zigzag carbon chains. Red and black lines denote α and β spin channel, respectively.

An important implication derived from Fig. 1(e) is that if the width of a ZGNR is sufficiently large, half-metallicity might be achievable even with weaker electron-donating group for edge modification. To confirm this postulation, we replaced the OH groups by H atoms for edge modification. As shown in Figs. 2(a) and 2(b) and Fig. S2 (see supplemental materials²⁰), the chemically modified 8-ZGNR is still a semiconductor with trivial spin-polarization, but the 72-ZGNR becomes half-metallic. Figure 2(c) and Fig. S3 (see supplemental materials²⁰) confirm that the band gap of β spin channel decreases with increasing n , and is closed when $n=72$, a critical value beyond which the ZGNR becomes half-metallic.

Next, we present a special design of chemical modification of graphene [Fig. 3(a) and Fig. S4], where periodically modified carbon strip includes four zigzag chains—two chains are modified with OH groups and another two with F atoms. The unmodified part (in a unit cell) has $m=16$ zigzag carbon chains. As mentioned above, this chemically modified graphene may be viewed as merging a series of edge modified 20-ZGNRs together. DFT geometric optimization shows that the chemically modified graphene exhibits a steplike structure [Fig. 3(a) and Fig. S4(a)]. Nevertheless, the computed electronic band structure [Fig. 3(b)] and DOS [Fig. S5(a)] indicate that the chemically modified graphene is also a half-metal, similar to the case of chemically modified 16-ZGNR. Moreover, as shown in Fig. 3(c), the α spin density is mainly localized around the carbon atoms adjacent to the OH groups while the β spin density is mainly localized around the carbon atoms adjacent to the F atoms. This be-

havior in spin-density distribution resembles that at the two edges of chemically modified ZGNR.^{12–17} Hence, these chemically modified carbon chains can be viewed as boundaries to effectively divide the graphene sheet into a series of identical ZGNRs. When the OH groups are replaced by H atoms on the graphene, as expected, the graphene is transformed back to a spin-polarized semiconductor due to the weaker electron-donating capability of H than OH groups. However, if the width of unmodified carbon part (in every unit cell) is increased to $m=72$, the graphene becomes half-metallic again [Fig. 3(d) and Fig. S5(b)],²⁰ similar to the 72-ZGNR case shown in Fig. 2(c). This result reinforces our view that as far as the half-metallicity is concerned, the chemically modified graphene can mimics behavior of edge modified ZGNRs.

In summary, we have studied electronic properties of ZGNRs and graphene modified by OH (or H) groups and F atoms. We show that (i) both can be converted to half-metals as long as the unmodified carbon part (or the width of ZGNR) is sufficiently wide, and (ii) the chemically modified graphene can mimic electronic behavior of edge modified ZGNR. Note that a recent study shows that ZGNRs produced by “cutting” graphene by hot plasmas may result in edge defects with impurities that can suppress spin polarization.²¹ The standard lithographic techniques may be less intrusive to the graphene structure than direct “cutting” for implementing flexible chemical modification, thereby converting graphene to a half-metal.

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