Semiconductor to Metal to Half-Metal Transition in Pt-Embedded Zigzag Graphene Nanoribbons

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Supporting Information

ABSTRACT: The electronic and magnetic properties of Pt-embedded zigzag graphene nanoribbons (Pt−ZGNRs) are investigated using density-functional theory calculations. It is found that Pt−ZGNRs exhibit a semiconductor−metal−half-metal transition as the position of Pt substitutional impurities in the ribbon changes from the center to edge sites. This behavior can be attributed to the interaction between Pt impurities and edge states of ZGNRs, which governs the electron occupation of the edge states. The transition always occurs independent of ribbon width. However, Pt impurity concentration is important for obtaining this transition. Our results demonstrate that Pt−ZGNRs can be used as versatile electronic devices.

1. INTRODUCTION

In spite of the many fascinating properties of graphene,1,2 such as relativistic massless dispersion and high mobility, the gapless band structure of graphene creates many challenges in some applications of this material, e.g., in logical nanodevices. Thus, it is highly desirable to develop a technique to tune the electronic structure of graphene and make it semiconducting. Investigations have indicated that an electronic gap in graphene systems can be opened by carving ribbons of a finite width from graphene sheets.3−5 The electronic structure of graphene nanoribbons (GNRs) and band gap value can be controlled by edge shape,6−8 as edge reconstructions lower the energy of the system,9,10 so that in principle one can obtain metals or semiconductors with the desired gap. More interestingly, zigzag GNRs (ZGNRs) are known to have localized edge states, which are antiferromagnetically coupled between the two edges.11−13 It is predicted that there are two most stable spin configurations, one with the spins at both edges being ferromagnetically (FM) coupled and another for which the spins are coupled antiferromagnetically (AFM). The AFM configuration is more stable than the FM one. It has been shown that the ferromagnetic ZGNRs are metallic, but the antiferromagnetic ZGNRs are semiconducting.6,14,15

The electronic properties of GNRs are sensitive to many factors, such as doping, edge modification, defect, and deformation.16−19 Among all the possibilities, impurity doping is one of the most frequently adopted ways for tuning the properties of graphene. For instance, the effects of transition metal atoms embedded in single and double vacancies on the electronic and magnetic properties of graphene have been theoretically studied.20 Chan et al. have analyzed the structural and electronic properties of 12 different metal adatoms on graphene.21 Rigo et al. have studied the structural, magnetic, and transport properties of a single Ni atom adsorbed on ZGNRs.22 Longo et al. have investigated the properties of Ni and Fe nanostructures on ZGNRs.23 A model was developed to describe how the energetics of the GNRs doped with a single impurity depends on the position of the impurity.24 Experimentally, metal atoms (Pt, Co, and In) have been successfully incorporated into graphene in substitutional positions using ion25 or electron-irradiation-mediated26 techniques. The effects of transition metals on the electronic doping and scattering in graphene have been investigated using molecular-beam epitaxy combined with in situ transport measurements.27

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Recently, Gan et al. observed Pt atom diffusion on a graphene surface and found that Pt atoms tend to move to the edge sites of graphene flakes.\textsuperscript{28} One can infer that the presence of Pt atom should also have a considerable effect on the properties of GNRs. Thus, it is important to understand the atomic structure, energetics, and electronic properties of Pt atoms on GNRs. Earlier theoretical studies\textsuperscript{19,24} provided many insights into the effects of the edges on the migration of gold atom on GNRs and helped to interpret the experimental results. In this paper, we also use first-principles calculations to study how Pt atom impurities influence the electronic properties of the ZGNR. We demonstrate that upon introduction of Pt impurities, the electronic properties of the ZGNR are remarkably modified, and the ZGNR exhibits a semiconductor–metal–half-metal transition as the position of Pt impurities changes from the center to edge sites. We further explain the transition through the interaction of Pt impurity and ribbon edge states.

2. METHOD AND MODEL

Calculations were performed using the Vienna Ab Initio Simulation Package (VASP) code\textsuperscript{30,31} based on density-functional theory (DFT). The exchange and correlations were described by the Perdew–Burke–Ernzerhof (PBE) functional\textsuperscript{32} under the generalized gradient approximation (GGA). The ion–electron interactions were treated with the projector augmented wave (PAW) approximation.\textsuperscript{33,34} The plane wave cutoff energy was set to 500 eV, and a higher value had little effect on the results. The structures were relaxed until the energy and the force on each atom were less than $10^{-5}$ eV and 0.01 eV/Å, respectively. A $15 \times 1 \times 1$ k-point mesh with Monkhorst–Pack scheme was used to sample the 1D Brillouin zone. The intervals between the ribbons were maintained at 15 Å for both layer–layer and edge–edge distances to simulate isolated ribbons.

Following an established convention,\textsuperscript{17} ZGNRs were characterized by the number of zigzag chains ($N$) across the ribbon width. In our study, we considered the case of $N = 8$ ZGNR as the typical system. All edge C atoms were saturated by H atoms to avoid dangling bonds. Doping was modeled in the supercell made of the four unit cells by substituting a Pt atom for a C atom in the ZGNRs. Eight different substitution sites were considered from the center to the edge of the ribbon, as indicated by the numbers (1–8) in Figure 1. For each of the considered configurations, full relaxation was performed, and the optimized configurations are presented in Figure S1 in the Supporting Information. In configurations 1–7, the Pt impurity forms three covalent bonds with the nearest C atoms, and the C–Pt bond length is from 1.93 to 1.95 Å, in accordance with previous calculations.\textsuperscript{20} In configurations 7 and 8, the Pt atom replaced the edge C atom, and the C–Pt bond length is from 1.91 to 1.98 Å. As the Pt atomic radius is larger than that of the C atom, the Pt atom is displaced outward from the ZGNR plane by a distance 1.40–1.94 Å.

3. RESULTS AND DISCUSSION

A. Electronic and Magnetic Properties of Pt–ZGNRs with Pt Impurity at Various Sites. To get insight into the relative stability of Pt–ZGNRs, the binding energies of Pt atom at different sites were calculated. The binding energies ($E_b$), defined as the difference between the energy of the Pt atom in the substitutional position of ZGNRs and the energy of the reconstructed single vacancy plus the energy of the isolated Pt atom, are presented in Figure 2. The typical values of $E_b$ vary from $-8.3$ to $-7.2$ eV, which suggests the high stability of the substitutional Pt atom in ZGNR. It means that Pt atom binds strongly to single vacancy, as reported previously for graphene.\textsuperscript{20} It is evident that the edge configuration (site 8) is energetically more favorable than the other sites. This indicates that the edge (site 8) of ZGNR is the most favorable site for Pt impurity.

In order to explore the modifications of the electronic and magnetic properties induced upon introduction of Pt impurities, we performed spin-polarized total energy calculations for the Pt–ZGNRs with the following three magnetic phases: (i) nonmagnetic state, denoted by NM; (ii) the antiferromagnetic state, with the ferromagnetically ordered spins at each edge, but with opposite directions of the spin localized on different edges, denoted by AFM; and (iii) the ferromagnetic state, with ferromagnetically ordered spins at each ribbon edge and the same spin directions between two edges, denoted by FM. The FM and AFM states were obtained by the electronic structure optimization starting with high initial values of the spins on the edge atoms. The relative energies of NM, AFM, and FM states for the Pt–ZGNRs are shown in Table 1. It is found that when the Pt atom is embedded at the ZGNR inner area (sites 1–5), we find that the AFM state is more stable compared to their corresponding FM state. On the

![Figure 1. Atomic structure of ZGNR with substitutional Pt impurities used in the simulations. The numbers (1–8) denote different substitution sites. The white and gray balls represent H and C atoms, respectively.](image-url)
contrary, for the edge configurations (sites 6–8), the coupling between the edge and the impurity leads to the same final state.

As evident from Table 1, when Pt atom is embedded at the inner sites (1–5), the total magnetic moment of the system is the same as for the pristine ZGNR (0 μB). However, for the edge configurations (6–8), the system acquires a finite magnetic moment upon introduction of the Pt impurity, which can be associated with the coupling between the edge and the impurity states. The effect of the Pt–edge coupling is evident from the spin densities in Figure 3. In fact, the spin densities

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**Table 1. Total Energies of NM, AFM, and FM States of Pt–ZGNRs, along with the Total Magnetic Moment of the Lowest Energy State for Each Configuration**

<table>
<thead>
<tr>
<th>site</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
</tr>
</thead>
<tbody>
<tr>
<td>E&lt;sub&gt;NM&lt;/sub&gt; (eV)</td>
<td>0</td>
<td>−0.04</td>
<td>0.01</td>
<td>−0.15</td>
<td>−0.01</td>
<td>−0.64</td>
<td>−0.67</td>
<td>−2.69</td>
</tr>
<tr>
<td>E&lt;sub&gt;AFM&lt;/sub&gt; (eV)</td>
<td>−0.25</td>
<td>−0.27</td>
<td>−0.24</td>
<td>−0.35</td>
<td>−0.23</td>
<td>−0.77</td>
<td>−0.81</td>
<td>−2.85</td>
</tr>
<tr>
<td>E&lt;sub&gt;FM&lt;/sub&gt; (eV)</td>
<td>−0.23</td>
<td>−0.26</td>
<td>−0.22</td>
<td>−0.34</td>
<td>−0.21</td>
<td>−0.77</td>
<td>−0.81</td>
<td>−2.85</td>
</tr>
<tr>
<td>μ&lt;sub&gt;tot&lt;/sub&gt; (μB)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1.28</td>
<td>0.35</td>
<td>0.35</td>
<td>0</td>
</tr>
</tbody>
</table>

*The NM state energy of the Pt atom at site 1 is set to zero.*

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Figure 3. Spin-density distribution of Pt–ZGNRs: (a) configuration 1, (b) configuration 6, (c) configuration 7, and (d) configuration 8. The isovalue for the blue and red isosurfaces are 0.005 and −0.005 e/Å³, respectively.

Figure 4. Band structures of Pt–ZGNRs and the corresponding charge densities of the states near the Fermi level at the X point for (a) configuration 1, (b) configuration 6, (c) configuration 7, and (d) configuration 8. The blue solid line and red dashed line denote spin-up and spin-down channels, respectively. The Fermi level is indicated by a horizontal olive dashed line. The isovalue is set to be 0.006 e/Å³.
polarization of the right edge is locally suppressed by the presence of the Pt atom for the edge configurations (Figure 3b–d). It is well-known that the spin polarization in ZGNR originates from the edge states at the Fermi energy. The interaction between the Pt atom and the right edge C atoms destroys the edge states and suppresses the spin polarization, which destroys the symmetry of spin distributions, consequently inducing the magnetic moment. The phenomenon is analogous to the effect of edge defects and impurities on the magnetic structure of ZGNRs.35 The edge magnetism suppression was also observed in Au- and Ti-embedded ZGNRs.36,37

To probe the effect of the position of the Pt impurity on the electronic properties of the ZGNR, we calculated the band structures for different configurations. The pristine 8-ZGNR has an AFM ground state and shows a band gap of 0.45 eV. Figure 4a shows the band structure of configuration 1. The system maintains its semiconducting character and has a band gap of 0.17 eV. It is well-known for the pristine ZGNR that the energy bands near the Fermi level are mainly associated with the edge states.6 The charge density analysis indicates that the lowest unoccupied spin-down state results from the edge C atoms, whereas the highest occupied spin-up state is mostly localized at the Pt and neighboring C atoms. Therefore, the occupied orbitals of the Pt atom and the neighboring C atoms have much higher energy than that of the edge C atoms, which contribute to the decrease of the band gap. The band structures of the system with impurities at other inner sites (2−5) are similar to that of configuration 1, which are presented in Figure S2 in the Supporting Information. All of them have semiconducting character; their band gaps are 0.13, 0.26, 0.16, and 0.26 eV for configurations 2−5, respectively. Configuration 6 exhibits a metallic character, and the charge densities are localized along the right edge C atoms. This corresponds to the occupation of the spin-up edge state, which is empty in the clean ZGNR and is promoted across the Fermi level as a consequence of the interaction with the Pt atom. Conversely, the corresponding occupied spin-down edge state tends to become half-occupied. In configurations 7 and 8, it can be seen from Figure 4c,d that the spin-up channel is semiconducting, while the spin-down channel is metallic with a band crossing the Fermi level. Thus, the system is half-metallic and able to provide 100% spin-polarized current. The charge densities originate from the Pt atom and the right edge C atoms. Different from configuration 6, the spin-up edge state is preserved at the conduction band, as well as the spin-down edge state across the Fermi level. Comparing the band structures for the different Pt sites, we can notice that the energy bands are much more affected when the separation between the Pt impurity and the edge decreases.

Usually, GGA exchange and correlation functionals underestimate the band gap of semiconductors. To assess their effects on the electronic structure of the doped ribbons, we performed test calculations with the hybrid HSE06 functional38−40 which could give more accurate results. Taking configuration 8 as an example, the band structure was calculated using the HSE06 functional and is presented in Figure S3 in the Supporting Information. The results show that its spin-up gap is increased from 0.13 to 0.17 eV, while the spin-down band preserved crossing the Fermi level. So configuration 8 remains half-metallic, confirming our results. Since the HSE06 calculations are computationally expensive while the GGA correctly describes the trends of the band gap in Pt−ZGNRs, we employ the GGA approach in the bulk of the calculations.

As mentioned above, the near-gap states of the pristine ZGNR mainly originate from the edge states. Thus, we can

![Figure 5. PDOS of Pt atom embedded at different sites of the ZGNR for (a) configuration 1, (b) configuration 6, (c) configuration 7, and (d) configuration 8. The red and blue lines indicate the PDOS of Pt atom and the right edge C atom. The positive and negative values represent spin-up and spin-down channels, respectively.](image-url)
understand the band structure transition from the edge effect. The projected density of states (PDOS) of the Pt atom and the right edge C atom is shown in Figure 5. For configuration 1, we did not observe interactions between the electronic states of the Pt atom and the right edge C atom around the Fermi level, as indicated in Figure 5a. The impurity Pt atom at the inner site hardly affects the edge states of the ZGNR, and the system preserves its semiconducting characteristic. Configuration 6 shows continuous PDOS around the Fermi level for both spin channels in Figure 5b, being responsible for the metallic character. For configuration 7, the environment of the Pt atom varies significantly, directly bonding to the right edge C atoms. Figure 5c shows that the hybridization between the Pt atom and the right edge C atom happened within an energy interval between 0 and 0.2 eV above the Fermi level, being almost zero. This dominates the half-metallicity. In configuration 8, the Pt atom directly replaced a right edge C atom, the PDOS is similar to that of configuration 7, and it also shows half-metallicity. Thus, the results indicate that the system exhibits semiconductor, metal, and half-metal transitions with respect to the position of Pt atom in the ZGNR.

**B. Dependence of the Electronic Properties on Ribbon Width.** We calculated the electronic structure of a series of Pt−ZGNRs with different widths and Pt-embedded sites, which include center sites (site 1), subedge sites (site 6), and edge sites (site 8), to test the dependence of the electronic properties on ribbon width, and the results are presented in Table 2. It is found that the system always exhibits the semiconducting character for the center-site-embedded Pt−ZGNRs. This can be attributed to the interaction between the Pt atom and the edge C atoms. When the Pt impurity is embedded at the center site, the interaction between Pt atom and edge C atoms is weak, which does not influence the edge states around the Fermi level. So ZGNR preserves its semiconducting character. For the subedge-site-embedded Pt−ZGNRs, all the systems display the metallic character independent of ribbon width. This indicates that the interaction between the Pt atom and the edge C atoms does not change with ribbon width. With the increase in the ribbon width, all edge-site-embedded Pt−ZGNRs display half-metallicity. Similar to the above cases, though ribbon width changes, the environment of the Pt atom replacing the edge C atom does not vary much. This transition trend is found to be independent of the ribbon width, pointing out that the ribbon showing the site-induced transition from semiconductor to metal then to half-metal can be used as an electric switch in nanodevices.

**C. Dependence of the Electronic Properties on Pt Impurity Concentration.** Furthermore, the effect of doping concentration has also been investigated by choosing different supercell sizes characterized by the number N of unit cells in the supercell. Here, we consider the cases of N = 3, 4, and 5, denoted as Pt−3ZGNR, Pt−4ZGNR, and Pt−5ZGNR, respectively. Taking the edge-site-embedded Pt−ZGNRs as an example, we calculated their band structures, and the results are shown in Figure 6. It is found that doping concentration is important for the electronic properties of Pt−ZGNRs. For a higher concentration of Pt impurity, Pt−3ZGNR presents semiconductor character. For a lower concentration of Pt impurity, Pt−5ZGNR demonstrates metal character. Only Pt−4ZGNR shows the half-metallicity. So the semiconductor to metal to half-metal transition in Pt−ZGNRs is sensitive to the Pt impurity concentration, and an appropriate doping concentration would be the key factor to realize this transition in Pt−ZGNRs.

**D. The Random Distribution of Pt Impurities in the Edge of ZGNRs.** As the incorporation of Pt impurities into the edges may be random in the experiments, we also studied the effects of a random distribution of Pt impurities at the edge of ZGNRs on the electronic structure. Three different configurations of Pt impurities in the edge of ZGNRs are considered and presented in Figure 7. It is found that its spin-up gap is 0.11, 0.10, and 0.07 eV, respectively, while the spin-down band preserved crossing the Fermi level. So the system remains half-metallic; the random distribution of Pt impurities in the edge of ZGNRs does not change the half-metallicity.

### 4. CONCLUSIONS

Using density-functional theory calculations, we have investigated the electronic and magnetic properties of Pt−ZGNRs. It is found that Pt impurities will considerably modify the band structure of the ZGNR and induce a semiconductor–metal–half-metal transition, depending on the position of Pt impurity in the ribbon. This behavior can be attributed to the interaction between Pt impurity and the edge states of ZGNRs. This transition can always be present, independent of the ribbon width. However, an appropriate doping concentration would be the key factor to realize this transition in Pt−ZGNRs.
results demonstrate that Pt–ZGNRs can be used as versatile electronic devices.

**ASSOCIATED CONTENT**

* Supporting Information
Optimized configuration of ZGNRs with Pt atom at different substitution sites, the band structures of Pt–ZGNRs for configurations 2–5, and band structures of the configuration 8 calculated by the GGA with PBE and HSE06 functional. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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