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# Graphene Nanoribbons: Geometric, Electronic, and Magnetic Properties

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## 1. Introduction

Graphene nanoribbons (GNRs) have one-dimensional structures with hexagonal two-dimensional carbon lattices, which are stripes of graphene. Their structures and their electronic and magnetic properties have been intensively studied both experimentally and theoretically. Due to their various edge structures, GNRs present different electronic properties ranging from normal semiconductors to spin-polarized half metals, which opens the possibility of GNRs as electric devices.

In this chapter, the geometric, electronic, and magnetic properties of GNRs are discussed. First, the electronic and magnetic properties of pristine GNRs are understood with their special structures. We emphasize the importance of one-dimensional quantum confinement effect and edge states. Secondly, since GNRs have large surface-volume ratio and special edge states, their properties can be modified by many methods, such as doping and adsorption. The electronic property and its response to modulation are described in detail. Finally, the experimental realizations of GNRs are introduced, which provide substantial bases to theoretical prediction of GNRs' electronic and magnetic properties. Possible future research directions are also discussed.

## 2. Magnetic and electronic properties of pristine GNRs

After the successful isolation of graphene, its amazing properties make it become a rising star of current materials research. However, as we know, graphene is a zero-gap semiconductor. To extend the real applications, an energy gap is needed, which enables the basic electric logic states: on and off. Besides, carbon-based magnetic materials are very important, which have small spin scattering and large potential to be immigrated into future electric devices. Due to the modern technology, etching or patterning graphene in some special direction has been realized. When graphene is etched or patterned along one specific direction, a novel quasi one-dimensional (1D) structure is obtained, which is a strip of graphene, referred as graphene nanoribbon (GNR). There are some critical questions about such GNRs: How do they organize the structures? Do they have energy gaps? And is there any magnetic state in these GNRs?

### 2.1 Geometric structures of pristine GNRs

The typical width of GNR is of nanometers. Different with 2D graphene, the termination in one direction introduces important quantum confinement effect (QCE), which endows GNR

various attractive properties. Depends on the termination style, normally, nonchiral GNR can be divided into two kinds: Armchair and Zigzag (Fig. 1 shows the structures of Armchair and Zigzag GNRs). Adopting the standard convention, the width of armchair GNRs is classified by the number of dimer lines ( $N_a$ ) across the ribbons. Likewise, the one of zigzag GNRs is classified by the number of zigzag chains ( $N_z$ ) across the ribbons. Perpendicular to the direction of defined width, GNRs repeat their geometric structures, and form one-dimensional periodic structures.

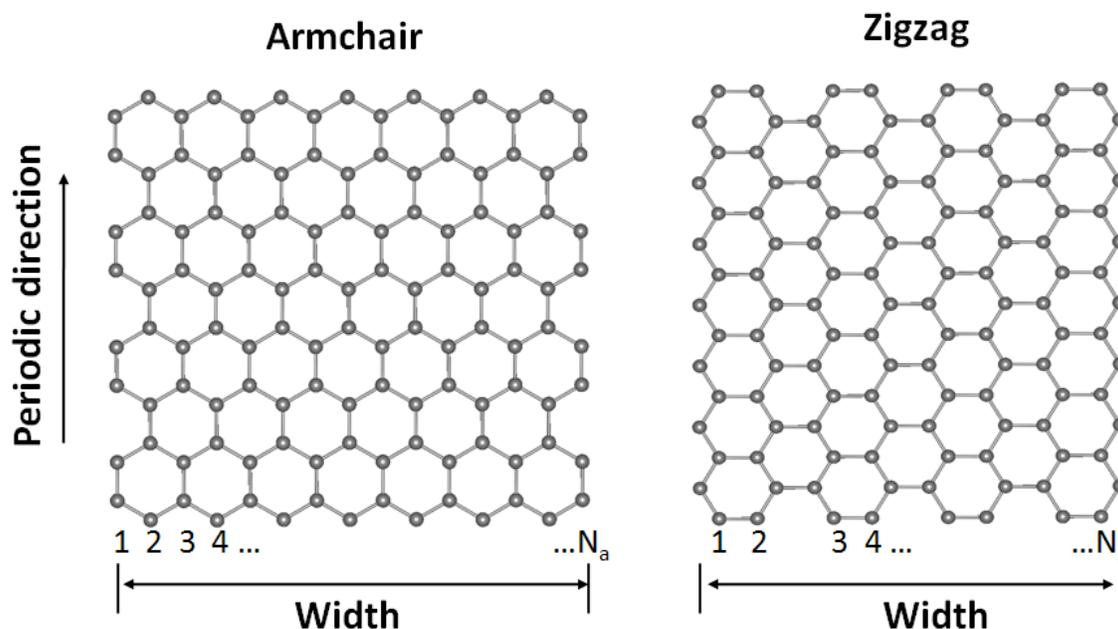


Fig. 1. Structure of armchair and zigzag nanoribbons

Since GNRs are stripes of graphene, edge atoms are not saturated. Active edge states become an important factor to determine the edge structures. For armchair GNRs, there is no any edge reconstructions, and the planar patterns are kept. While for zigzag GNRs, it is unexpectedly found that the zigzag edge is metastable, and reconstructions spontaneously take place at high temperature. Some special structures have been proposed as possible reconstructed patterns (Koskinen et al., 2008), however the detailed reconstructions still need to be further studied. To keep the planar structures of zigzag GNRs, hydrogen atoms are introduced to saturate the edge atoms of GNRs. Besides, in most of the reported structures in experiments, GNRs are found no reconstructions. Thus, most theoretical research has taken the saturated GNRs as the starting point. In the following context, edge atoms of GNRs are saturated by hydrogen atoms without special notation.

## 2.2 Electronic properties of Armchair GNRs

Many theoretical studies have been devoted into investigating the electronic properties of Armchair GNRs, such as tight-binding calculations, density functional theory (DFT) calculations, and many-electron green's function approach within GW approximation. Among those methods, DFT calculations adopt parameter-free self consistent field calculations, and their reliability has been broadly proved in solid state field and nano-scale systems. Thus, most of the theoretical investigations have been carried out with DFT calculations. However, it is well established that DFT calculations underestimate band gaps.

Other methods, such as GW approximation, have been adopted to correct DFT calculations, and get the reliable band gaps. In the following discussions, both DFT and GW results are included.

As shown in the Fig. 1, armchair GNRs are defined by the number of dimer lines ( $N_a$ ) across the ribbons. Their electronic structures have been carefully investigated by DFT calculations (Son et al. 2006a). Their results show that all armchair GNRs are semiconductors with energy gaps, which decrease as a function of increasing ribbon widths. No magnetism has been found in armchair GNRs. As seen from Fig. 2, the energy gaps as a function of ribbon width are well separated into three different kinds:  $N_a = 3p$ ,  $3p+1$ ,  $3p+2$  ( $p$  is integer). Moreover, the gap size hierarchy is well separated.  $N_a = 3p+1$  categories has the largest energy gap, while the  $N_a = 3p+2$  series is the smallest one.

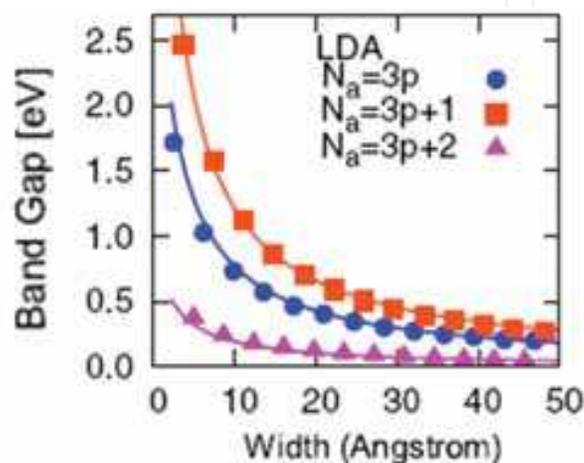


Fig. 2. The variation of band gaps of armchair GNRs with DFT calculations (Son et al. 2006a).

Armchair GNRs show semiconducting behaviours with a direct energy gap. The determining factor comes from the quantum confinement effect (QCE), which can be characterized by [energy gaps] versus [width]<sup>-1</sup>. Besides the QCE, son et al. has pointed that the edge effects play an important role to force the armchair GNRs to be semiconductors (Son et al. 2006a). As discussed in the previous parts, the edge carbon atoms of armchair GNRs are passivated by hydrogen atoms, which leads to the bonding of carbon atoms at the edges different with other carbon atoms. As a consequence, the bond lengths of carbon atoms at the edges are shorter than that in the middle of ribbons, and open the energy gaps of armchair GNRs.

Although armchair GNRs have three typical families (corresponding to  $N_a = 3p$ ,  $3p+1$ ,  $3p+2$ , respectively) with distinguished energy gaps, they have similar band shapes. As an example, the band structure of armchair GNR with  $N_a = 13$  is shown in Fig. 3. (Sun et al. 2008), there are four important subbands which dominate the electronic behaviors of armchair GNRs. These subbands are constituted by the  $\pi$  bonds of carbon atoms, and have different shapes, which provide the possibility of external modulations, such as strain.

On the other hand, although DFT calculations can provide the correct qualitative pictures, the accurate energy gaps of armchair GNRs are needed. To solve the band-gap problems, Li et al. have performed first-principles calculations using many-electron Green's function approach within the GW approximation, which is treated as one of the most accurate methods to predict the energy gaps. It is clear that GW calculations give the same hierarchy

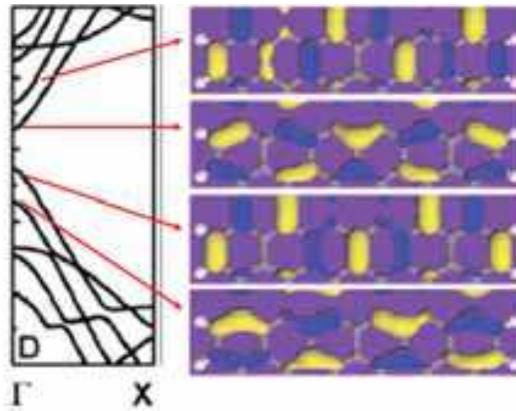


Fig. 3. Band structure and the space charge distribution of armchair GNRs ( $N_a = 13$ ) (Sun et al. 2008).

as those obtained in DFT calculations. But the GW corrections to the band gaps of armchair GNRs are significant. The corrections are from 0.5 to 3 eV for the GNRs with width from 1.6 to 0.4 nm (Li et al. 2007). Thus, GW calculations show that armchair GNRs can have large energy gaps with limited widths.

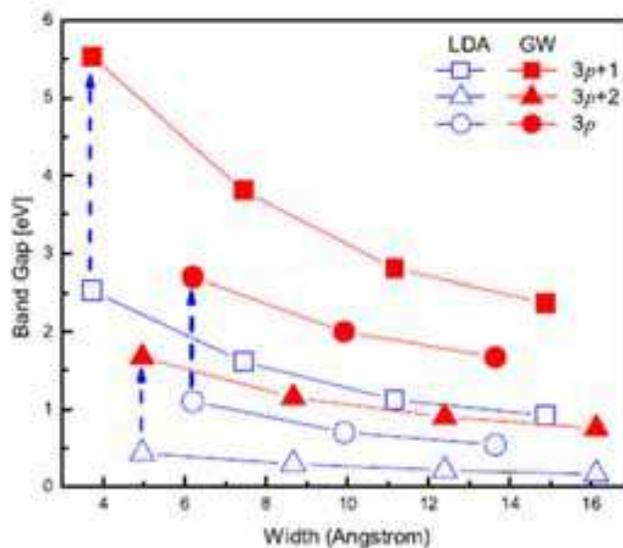


Fig. 4. The variation of band gaps of armchair GNRs with GW calculations (Li et al. 2007).

### 2.3 Electronic and magnetic properties of zigzag GNRs

For nanoribbons with zigzag shaped edges, without considering spin states, DFT calculations have shown that a set of doubly degenerate flat edge-state bands at Fermi level ( $E_F$ ) (Son et al. 2006a; Wu et al. 2009), which give rise to a very large density of states (DOS) at  $E_F$ . This DOS peak at  $E_F$  is half filled, which therefore provides Stoner instability leading to magnetic states.

By inclusion of the spin degrees of freedom within DFT methods, the zigzag GNRs have been predicted to have a magnetic insulating ground state with ferromagnetic ordering at each zigzag edge, and antiparallel spin orientation between the two edges (Son et al. 2006a; Wu et al. 2009). Different with armchair GNRs, the zigzag GNRs have the same hierarchy of band gap-width relationship.

In Fig. 5., the spin-density plot clearly shows that spin moments are mainly distributed at the edge carbon atoms. Compared with the nonspin-polarized solutions, spin-polarized edge states are more favoured, and the total energy difference between these states increases with the width of GNRs. For example, the energy difference is 20 meV per edge carbon atoms for  $N_z = 8$ , while becomes 24 meV for  $N_z = 16$  (Son et al. 2006a; Wu et al. 2009). Moreover, the spin-polarized states are further stabilized by ferromagnetic coupling at the edge, while antiferromagnetic coupling between the two edges. However, the energy difference between ferromagnetic and antiferromagnetic coupling is very small, and decreases as width of ribbons increases. When the width is significantly larger than the decay length of the spin-polarized edge states, antiferromagnetic and ferromagnetic states almost have the same stability (Son et al. 2006a; Wu et al. 2009).

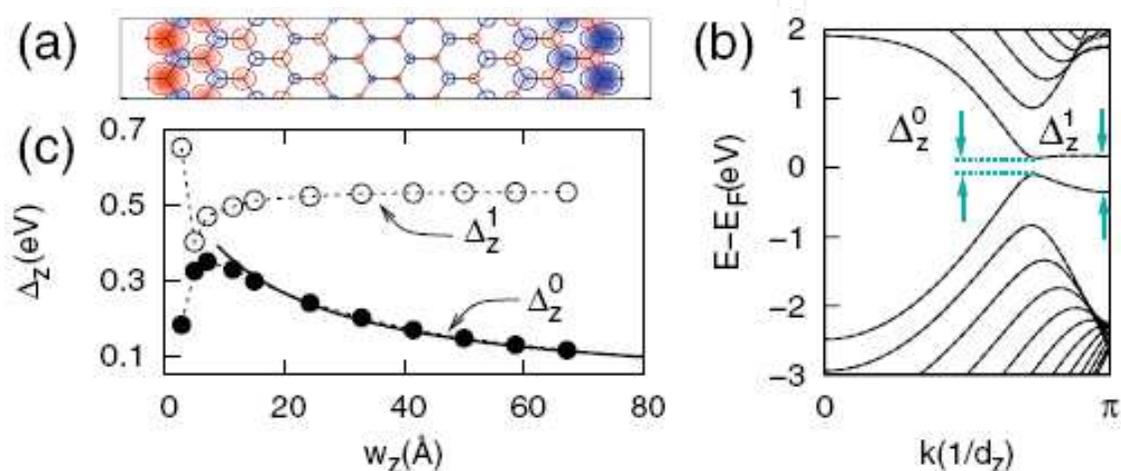


Fig. 5. (a) Spin density for zigzag GNRs with  $N_z = 12$ , red and blue mean different spin direction. (b) The band gaps of zigzag GNRs with  $N_z = 12$ , spin-up channel is degenerate with spin-down channel in all energy bands. (c) The variation of band gap and energy splitting as function of the width of zigzag GNRs. (Son et al. 2006a).

GW approach has large effect on such localized states in zigzag GNRs. Li et al's results show that the magnitudes of the corrections to the DFT energy gaps in zigzag GNRs are similar to those in AGNRs (Li et al., 2007). As plotted in Fig. 6., the corrections enlarge the band gap by roughly 1 eV for the studied ribbons. On the other hand, the spin-polarized edge states are kept.

Based on the above results, it is clear that DFT method can correctly predict the qualitative properties of zigzag GNRs, namely, spin-polarized edge states and semiconducting with direct energy gaps. However, GW approach and similar methods can provide better quantitative results. In this sense, DFT calculations as a simple method will provide reliable physical pictures in most cases, and satisfy our requirements in studying GNRs.

### 3. Magnetic and electronic properties of GNRs under external modulations

As discussed above, both armchair and zigzag GNRs have direct band gaps. Compared with graphene, which is a zero-gap semiconductor, the insulating behaviour of GNRs is very important. It is well known that two distinguished states, metallic and insulating states, are necessary to develop reliable electric devices. Thus, for the potential applications based on graphene, GNRs greatly extend the functionality of graphene.

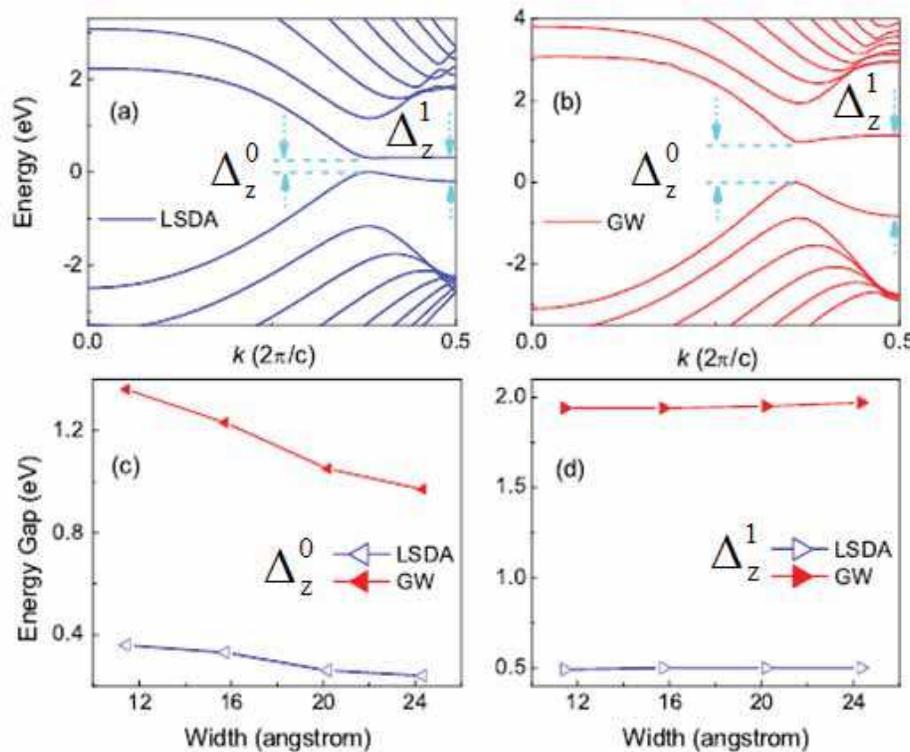


Fig. 6. Calculated band structure of zigzag GNRs with  $N_z = 12$  for (a) DFT calculations and (b) GW calculations, respectively. (c) and (d) represent the variation of direct band gap and energy gap at the zone boundary with the width of zigzag GNRs (Li et al. 2007).

On the other hand, because of the existence of edges in GNRs, there are many possibilities of external modulations to modify the electronic and magnetic properties of GNRs, such as applying electric field, strain, and edge modifications. Besides, the special geometric and electronic structures of GNRs provide the potential possibilities of producing graphene-based spintronics. As we know, zigzag GNRs have the spontaneous spin-polarized edge states. Thus, how to manipulate the electronic and magnetic properties of GNRs becomes a very interesting topic.

In the following part, we will discuss the reported external modulations on the armchair and zigzag GNRs. Since the pristine armchair GNRs are non spin-polarized materials, we discuss the reported results of armchair GNRs under external modulations first. While for zigzag GNRs, the situations are more complicated and interesting because of the spin-polarized solutions.

### 3.1 Armchair GNRs

#### 3.1.1 Applying strain

Armchair GNRs show semiconducting behaviours with a direct energy gap, and are well separated into three categories. To build future nano devices based on GNRs, the capability to control GNRs' electronic properties is highly desirable. One of the possible and effective ways is to apply external strain. Thus, how are the geometric structures and the related electronic structures deformed under external strain becomes interesting problems.

Sun et al. have carried out comprehensive DFT studies to investigate those problems (Sun et al. 2008). To clearly indicate such effect, the deformation of armchair GNRs can be

represented by the strain ( $\varepsilon$ ), defined as  $\varepsilon = (r - r_0) / r_0$ , where  $r$  and  $r_0$  are the deformed and initial equilibrium lattice constants ( $r_0 = 4.287 \text{ \AA}$ ) along the periodic direction of armchair GNRs. As we know, the structures of armchair GNRs are deformed to release the strain energy by applying external strain. In order to describe the vibration of C-C bonds in GNRs, four representative C-C bonds are selected in armchair GNRs with  $N_a = 13$  (sketched in Fig. 7.). It is clear that the C-C separations change almost linearly with the strain, and the deformation leads to the largest change in the inner C-C bond length ( $a_1$ ). As reported in the pristine armchair GNRs, the C-C bonds ( $a_3$  and  $a_4$ ) are shorted because of the edge effect. Therefore, the stronger C-C bonds ( $a_3$  and  $a_4$ ) have smaller response under the same external strain tensor. Here we should note all armchair GNRs have the same tendency, which represents the general physical picture of armchair GNRs under external strain.

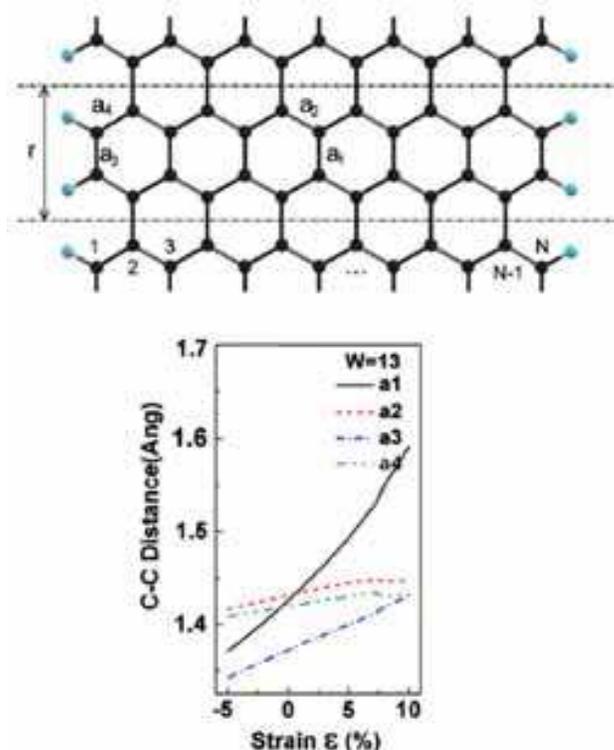


Fig. 7. The top one is the schematic of armchair GNRs with  $N_a = 13$ , four representative C-C bonds are shown, while the bottom one is the vibrations of C-C bond lengths under external strain (Sun et al. 2008).

Next, let us turn to the energy gap modification. Because armchair GNRs have three different categories, Sun et al. have selected  $N_a = 12, 13, 14$  as the representative ones to investigate this issue. As shown in Fig. 8., the calculated maximal energy gaps for the armchair GNRs with  $N_a = 12, 13, 14$  appear at  $\varepsilon = 5.0\%, -0.8\%$ , and  $9.5\%$ , respectively. While the minimal energy gaps occur at  $\varepsilon = -4.5\%, 7.3\%$ , and  $1.3\%$ , respectively. The shapes of the calculated curves display a zigzag feature for  $N_a = 12, 13, 14$ , which indicate that the energy gap is sensitive to the external strain.

To extend the studied widths, the variations of the energy gaps of three families of structures with different widths are plotted in Fig. 8. Sun et al. have summarized several features: (1) The minimal energy gaps of all deformed armchair GNRs are of the order of several meV. (2) The zigzag feature is observed in all deformed armchair GNRs (Sun et al. 2008).

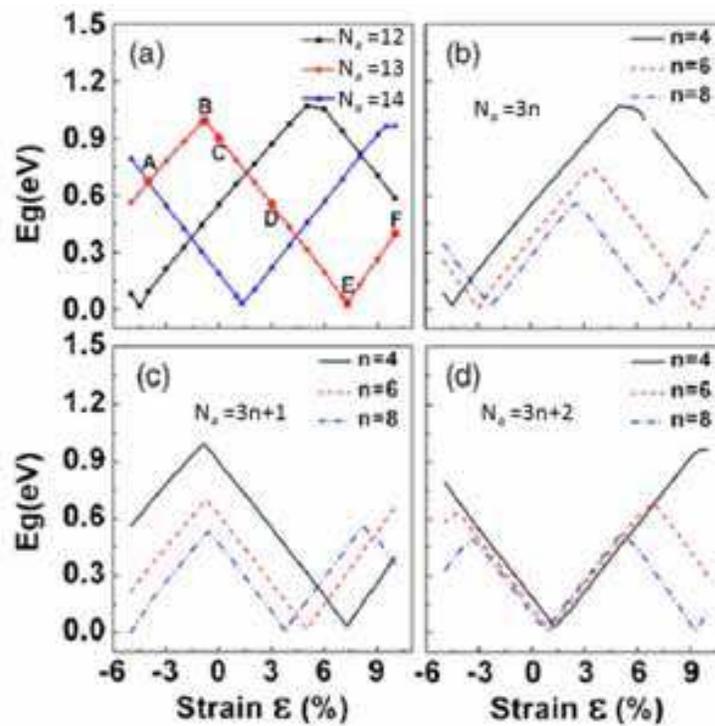


Fig. 8. (a) Variation of the energy gaps as a function of strain for the armchair GNRs with  $N_a = 12, 13, 14$ . (b), (c), and (d) are variation of energy gaps for three different categories (Sun et al. 2008).

### 3.1.2 Chemical adsorption

Armchair GNRs are non-spin-polarized semiconductors, therefore, how to produce armchair GNRs-based spintronics becomes an interesting question. Similar with carbon nanotubes, chemical adsorption of transition-metal (TM) atoms may be a possible solution. Kan et al. have proposed that armchair GNRs can be adsorbed by one-dimensional TM chains, leading to the desired magnetism (Kan et al. 2007a).

During their studies, they selected  $N_a = 10, 11, 12$  to represent the three different categories, and titanium chains are taken as the source of magnetism. To investigate the adsorptive behaviours, three different concentrations of adsorption have been considered, namely, one, two, and four Ti atoms per two unit cell. As shown in Fig. 9, Ti atoms are found to prefer the hollow sites near the edges, and form zigzag atomic chain (Kan et al. 2007a). The same tendency is observed for all three categories of GNRs. Their results indicate that Ti atoms will spontaneously produce one-dimensional atomic chains on GNRs under thermal equilibrium.

Since atomic Ti chains can form stable adsorption on GNRs, there are two natural questions: Do the hybrid structures have magnetic signals? And do they have special electronic structures? To answer these questions, Kan et al. have performed comprehensive theoretical studies within the DFT framework. The following results show all the hybrid structures (three different concentrations) are spin polarized with ferromagnetic coupling. For example, in the case of four Ti atoms per two unit cell, ferromagnetic states are lower in energy than antiferromagnetic states by 0.16, 0.16, and 0.14 eV for  $N_a = 10, 11, 12$ , respectively. The large energy difference of different magnetic coupling ensures the survival of ferromagnetism under high temperature.

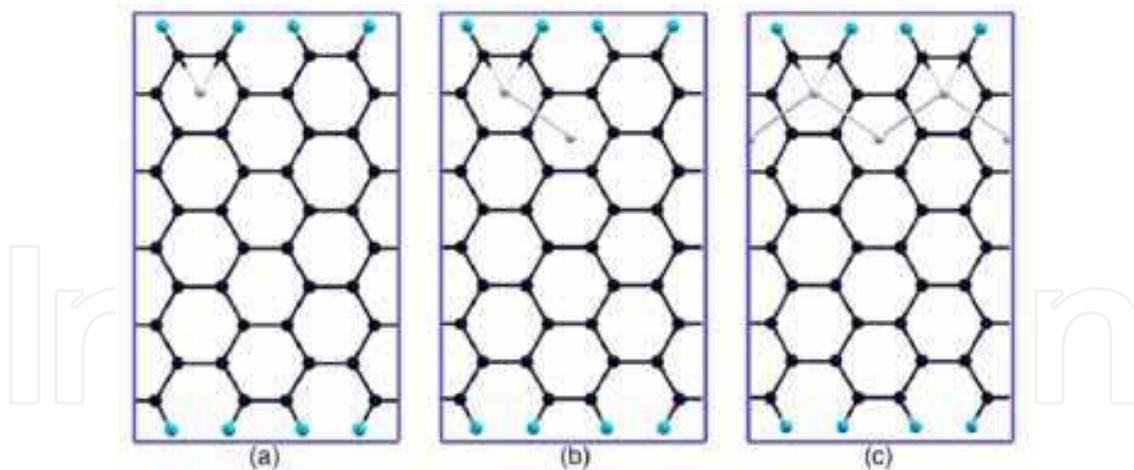


Fig. 9. (a) The geometric structures of armchair GNRs adsorbed by Ti chains under three concentrations, namely, (a) one Ti atom per two unit cell, (b) two Ti atoms per two unit cell, and (c) four Ti atoms per two unit cell. Black balls are C atoms, white balls are Ti atoms, and small blue spheres are H atoms (Kan et al. 2007a).

In Fig. 10., the calculated band structures of the hybrid structures are plotted. It is clear that their electronic structures show spin-selective characters. Especially, for  $N_a = 10$ , and 11, the band structures show perfect half-metallic behaviours.

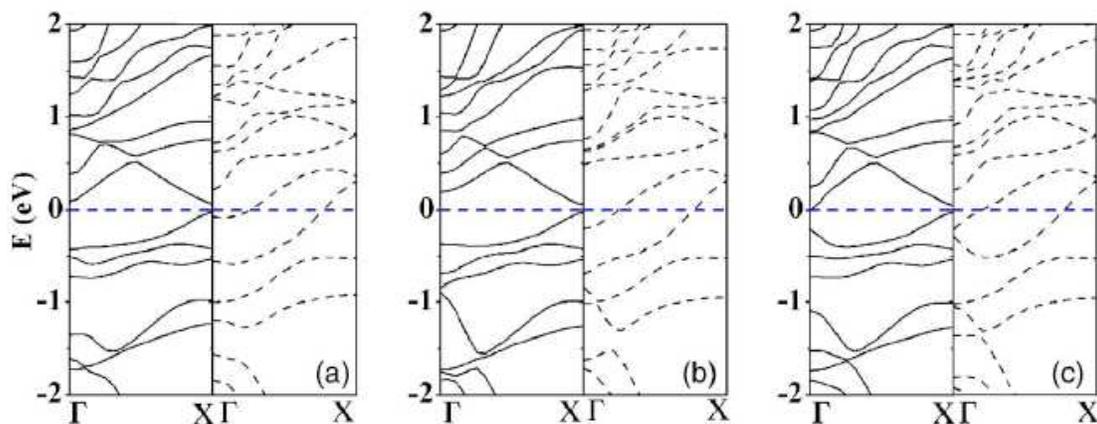


Fig. 10. Band structures of Ti atoms adsorptive GNRs for (a)  $N_a = 10$ , (b)  $N_a = 11$ , and (c)  $N_a = 12$ , respectively. The adsorptive structures are sketched in Fig. 9c. Solid lines represent spin-up channel, while dot lines mean spin-down channel (Kan et al. 2007a).

To find the tendency of electronic structures, Kan et al. have extended their research in hybrid GNRs with different widths. They concluded that all the adsorbed Ti chains are ferromagnetic, and the hybrid structures show metallic character. Moreover, they found that hybrid structures of GNRs and Ti chains present the half-metallic properties when the width of ribbons is smaller than 2.1 nm. Thus, this research paves a new way to explore spintronics at the nanometer scale based on GNRs.

### 3.2 Zigzag GNRs

#### 3.2.1 Applying electric field

It is now well known that zigzag GNRs are semiconductors with two localized electronic edge states. These two states are ferromagnetically ordered at each edge, and

antiferromagnetically coupled each other, which means the total spin of zigzag GNRs is zero. Since these states are edge states, the effects of external transverse fields are expected to be significant.

Son et al. have investigated the aforementioned problems by performing DFT calculations. In their research, the external transverse fields are simulated by a periodic saw-tooth-type potential, which is perpendicular to the direction of the ribbons edge. Taking  $N_z = 16$  as a representative model, Son found that the valence and conduction bands associated with one spin orientation becomes closer, and eventually close their gap under strong enough external electric fields. Whereas band gaps of the other spin orientation are widen. As shown in Fig. 11, spin-degenerate band structures become spin-selective, and eventually changed into half metals by applying external electric fields (Son et al, 2006b).

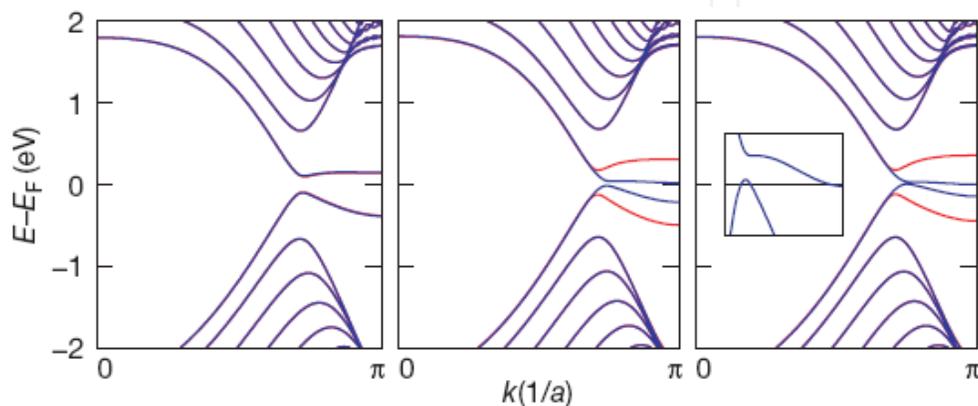


Fig. 11. From left to right, the spin-resolved band structures of zigzag GNRs with  $N_z = 16$  under electric fields 0.0, 0.05 and 0.1 V/Å, respectively. The red and blue lines denote bands of different spin channels (Son et al, 2006b).

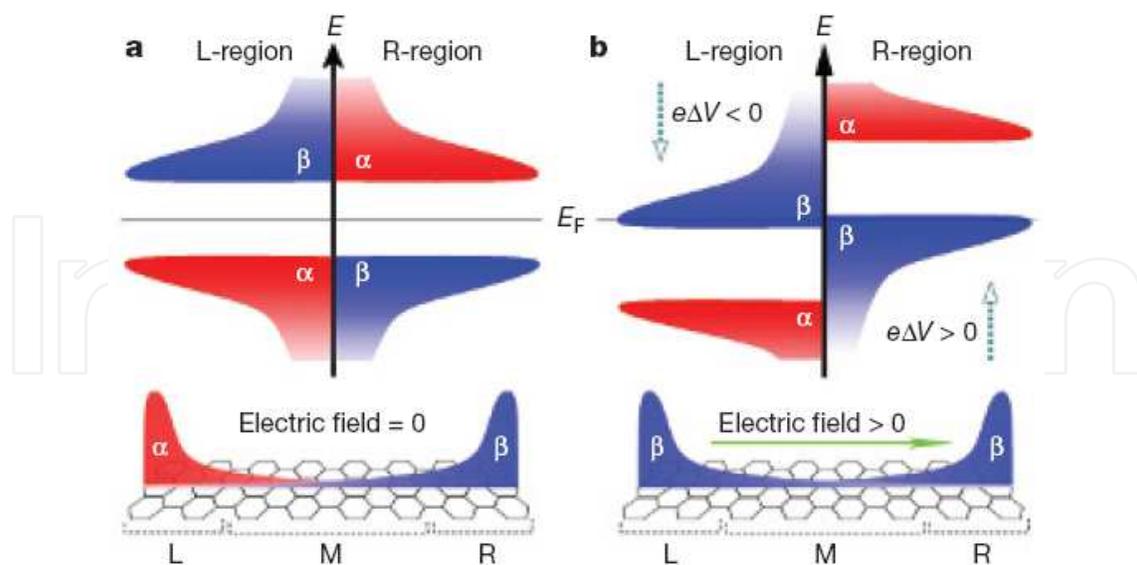


Fig. 12. (a) Schematic density-of-states diagram of the zigzag GNRs without external electric field. L-region (R-region) means the left (right) side of GNRs, and  $\alpha$  and  $\beta$  are two spin channels. (b) Density-of-states diagram under applied electric field (Son et al, 2006b).

The half-metallic property originates from the fact that the applied electric fields induce energy-level shifts of edge states. Based on the analysis of density of states, Son et al. have

used a simple model to explain the appearance of half-metallic property. As shown in Fig. 12, the spin-polarized states localized at two edges (left and right edges) are well spatially separated and degenerate in energy without applying electric fields. Since both occupied and unoccupied states of one special spin channel are located at the opposite sides of the zigzag GNRs, the effect of external electric field on them is different, namely, raising the energy-level of occupied, while lowering the one of unoccupied. Consequently, the energy gaps of one spin channel will be closed by external electric field, while leaving the other ones insulating. Thus, the half-metallicity comes from the relative movement in energy of edge states under electrostatic potential (Son et al, 2006b).

However, for any potential applications, the strength of critical electric field is very important. As we know, the semilocal DFT theory can only predict the qualitative band gaps. Thus, how strong does the electric field need to induce the half-metallicity becomes a mysterious. To solve the problems, Kan et al. have performed hybrid density functional calculations (B3LYP), which is viewed as one of the most accurate methods to get the quantitative results (Kan et al, 2007b). Their B3LYP calculations reproduce the half-metallicity under electric fields, but the critical electric fields are much higher than those from normal DFT calculations.

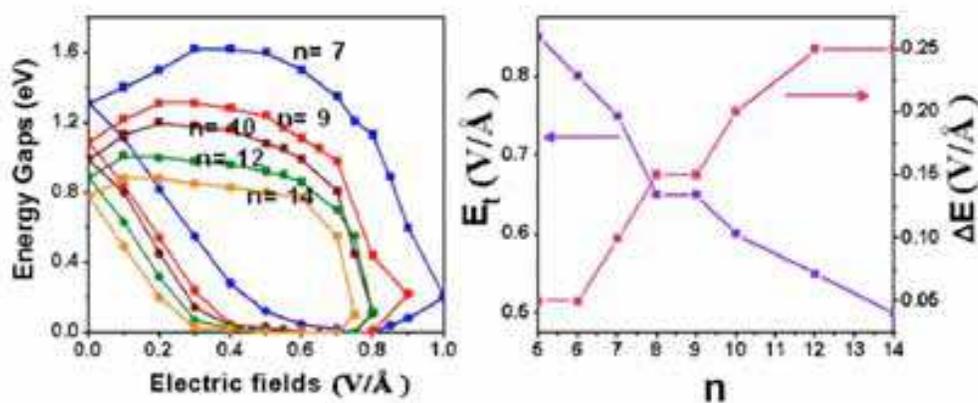


Fig. 12. Left: Band gaps of zigzag GNRs against external electric fields,  $n$  means the width of ribbons. The line with squares are spin-up channel, while filled circles are spin-down one. Right: The critical electric fields ( $E_c$ ) to achieve half-metallicity and the range of electric field strength to keep half-metallicity (Kan et al, 2007 b).

As shown in Fig. 12, the critical electric fields decrease with the increasing of ribbon widths. However, it is still too high for applications. On the other hand, the electric field range at which zigzag GNRs remain half-metallic increases with the ribbon width. All these results indicate that the half-metallicity induced by electric fields is robust, and independent on the theoretical methods adopted. Thus, the only problem is how to overcome the obstacle of high critical electric field in applications.

### 3.2.2 Edge modifications

Since spin-polarized edge states dominate the electronic and magnetic properties of zigzag GNRs, the edge modifications play an important role. To achieve the amazing half-metallicity, Kan et al. have proposed that edge modifications by chemical groups can overcome the obstacle of high electric field (Kan et al, 2008a). The designs are neat and simple as sketched in Fig. 13.

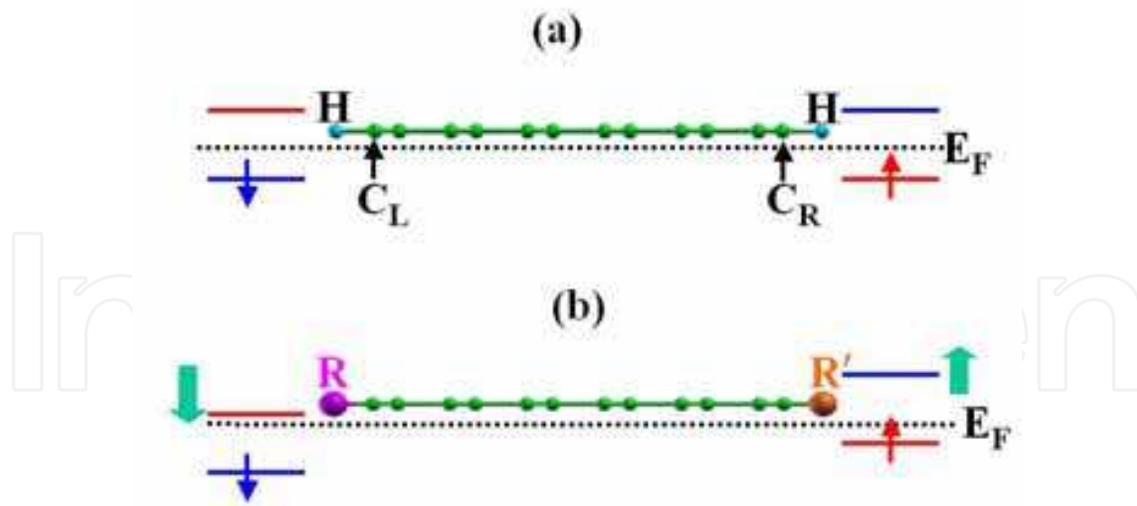


Fig. 13. (a) Structures of the H-saturated zigzag GNRs and schematic energy diagram for the edge states. (b) Schematic edge-state energy diagram of zigzag GNRs with different chemical modifications at two edges. (Kan et al, 2008a).

As we know, when zigzag GNRs are symmetrically saturated by hydrogen atoms at two edges, the spin-polarized edge states are degenerated in energy. One edge is occupied by spin-down electrons, while the other one is occupied by spin-up electrons. However, when the two edges are anti-symmetrically modified with different chemical groups, as shown in Fig. 13b, the induced potential shifts at two edges are different, which breaks the degeneracy of energy level of two edge states. Therefore, the modified ribbons become spin selective. Once the induced potential difference is large enough, the energy gap of one spin channel is closed, and zigzag GNRs are expected to become half metals.

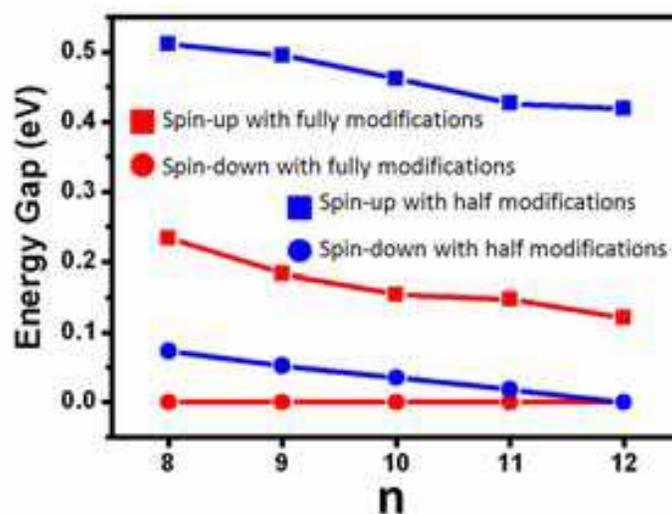


Fig. 14. The band gaps of zigzag GNRs with edge modifications. (Kan et al, 2008a).

To confirm the above predictions, Kan et al. performed DFT calculations to study the effect of different chemical groups (Kan et al, 2008a).  $\text{NO}_2$  and  $\text{CH}_3$  are selected as the typical groups achieving the half-metallicity. In order to study the effect of chemical modifications, two concentrations are considered, namely, fully and half modifications. As the definition, fully modifications mean that all the carbon atoms at one edge are modified by  $\text{NO}_2$ , while

the carbon atoms at the other edge are saturated by  $\text{CH}_3$ . For half modifications, the selected chemical groups and hydrogen atoms alternatively saturate the carbon atoms at two edges. As plotted in Fig. 14, the calculated band gaps show perfect spin-selective behaviours. For both fully and half modifications, half-metallicity can be achieved with enough width. Similar with Kan et al's works, Wu et al. reported that half-metallicity can be obtained by other chemical groups, such as OH groups at one edge, while  $\text{NO}_2$  or  $\text{SO}_2$  at the other edge (Wu et al, 2010). They have studied many chemical groups, and given many possibilities to future research. Thus, edge-modification has been viewed as a powerful tool to tail the electronic structures of GNRs.

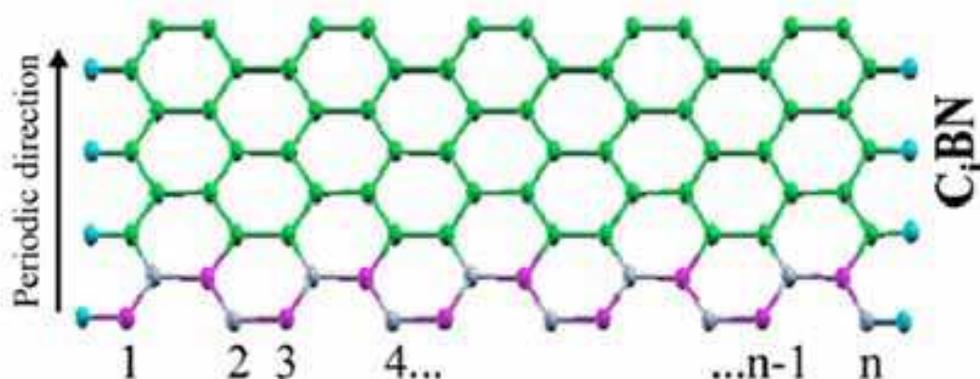


Fig. 15. The atomic structures of hybrid BCN nanoribbons. Green, pink, gray, and sapphire balls denote carbon, boron, nitrogen, and hydrogen atoms, respectively (Kan et al, 2008b).

### 3.2.3 Chemical doping

Since half-metallicity can be achieved with anti-symmetrical potential at two edges, doping boron and nitrogen atoms in zigzag GNRs becomes one possible way. Kan et al. has proposed one interesting model, as shown in Fig. 15 (Kan et al, 2008b). BN chains are integrated into zigzag GNRs, and each BN chain is well separated by  $n$  carbon chains ( $n = 1, 2, 3$ ). As we know, boron and nitrogen atoms provide holes and electrons when they are separately doped into zigzag GNRs. Therefore, the effect on the edge states of boron and nitrogen atoms definitely are different, which may induce half-metallicity.

To confirm their proposal, Kan et al. carefully studied the electronic structures of such hybrid BCN nanoribbons with DFT methods (Kan et al, 2008b). As the direct index, spin-resolved energy gaps are sketched in Fig. 16. There are three significant characters: firstly, all studied hybrid BCN nanoribbons, namely,  $\text{C}_1\text{BN}$ ,  $\text{C}_2\text{BN}$ , and  $\text{C}_3\text{BN}$ , are spin-selective materials when  $N_z$  is larger than 8. Secondly, all the studied BCN nanoribbons become half metals with enough width of ribbons. Thirdly, the critical width realizing half-metallicity is different. For  $\text{C}_1\text{BN}$ , the critical width is  $N_z = 12$ , while 10 and 8 for  $\text{C}_2\text{BN}$ , and  $\text{C}_3\text{BN}$ , respectively. In another words, the critical width decreases with the increasing of intervened carbon chains. These results mean that half-metallicity in hybrid BCN ribbons can be easily realized by controlling the doping methods of BN chains.

Similar with Kan et al's results, Dutta et al. have proposed that doping boron and nitrogen atoms into zigzag GNRs can lead to half-metallicity (Dutta et al, 2009). Slightly different with Kan et al's idea, Dutta et al. suggested that doped BN chains are perpendicular to the periodic direction. However, the electronic behaviours of doped BN chains are similar with the reported results of Kan et al.

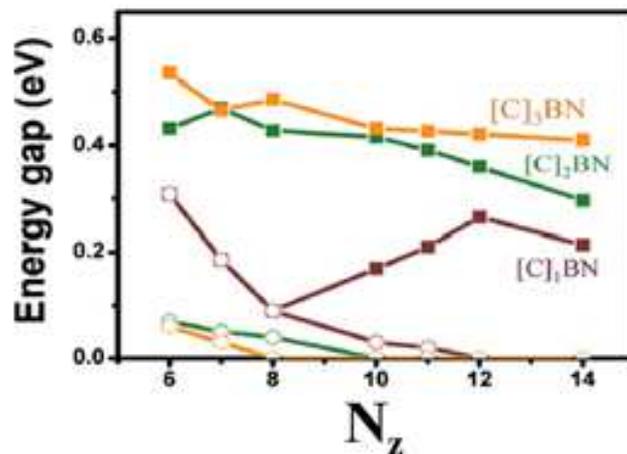


Fig. 16. The spin-resolved band gaps of hybrid BCN nanoribbons (Kan et al, 2008b).

### 3.2.4 Chemical adsorptions

Although the half-metallicity can be obtained by many methods, such as the electric field, edge modifications, and doping, we should keep in mind that the whole nanoribbons have no net magnetic moments. In applications of nano devices and spintronics, large net magnetic moments are sometimes desirable. On the other hand, transition-metal free magnetism is also interesting because of the weak spin-orbit coupling. Thus, the next important question is how to get large magnetic moments in such nanoribbons without magnetic atoms. To handle this problem, Kan et al. have theoretically suggested that zigzag nanoribbons have a large magnetic moment by adsorbing main-group atoms. In their studies, they used boron, carbon, and nitrogen atoms as adatoms (Kan et al, 2010).

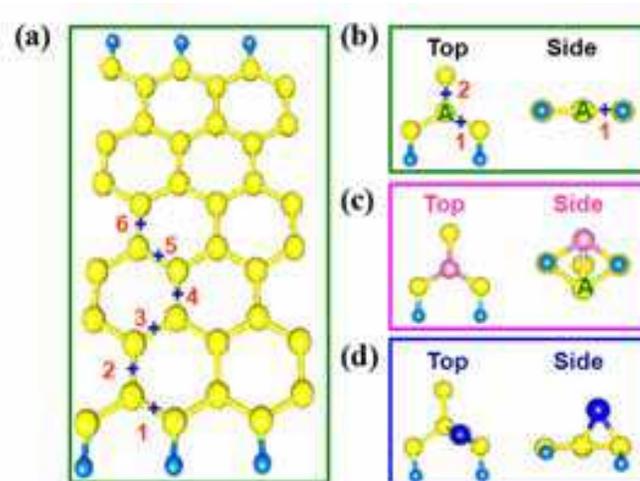


Fig. 17. (a) The possible adsorptive sites of zigzag GNRs. (b) The edge structures of pristine zigzag GNRs. The adsorptive structures for (c) boron (carbon) and (d) nitrogen adatoms (Kan et al, 2010)

As we know, zigzag GNRs are antiferromagnetic coupling between two edges, leading to net magnetic moments as zero. By adsorbing atoms, the bonding of pristine zigzag GNRs is broken, which may result in local states. Thus, the first question is how these adatoms bond with the zigzag GNRs. Using DFT calculations, Kan et al. found that the preferred adsorptive sites are near the edges. As shown in Fig. 17, they took zigzag GNRs with  $N_z = 6$

as an example, and considered all possible adsorptive sites. For boron and carbon, the adatoms prefer the site labelled as “A” in the figures, and push the original carbon atoms out of the plane of ribbons, while for the nitrogen atom, it prefers the site 1, which gives the lowest energy. The different adsorptive behaviours can be due to the strong tendency of  $sp^3$  hybridization in boron and carbon atoms.

The next question is whether adatoms can induce large magnetic moments. Luckily, the following studies give a positive answer. As seen in Fig. 18, the plotted spin density clearly shows that antiferromagnetic distributions of pristine have been switched into ferromagnetic distributions after carbon adsorption, which leads to a net magnetic moment of  $2 \mu_B$  per carbon adatom. While for boron and nitrogen adatoms, they have the same tendency with carbon adatoms, but the inducing magnetic moments are  $1 \mu_B$  per adatom.

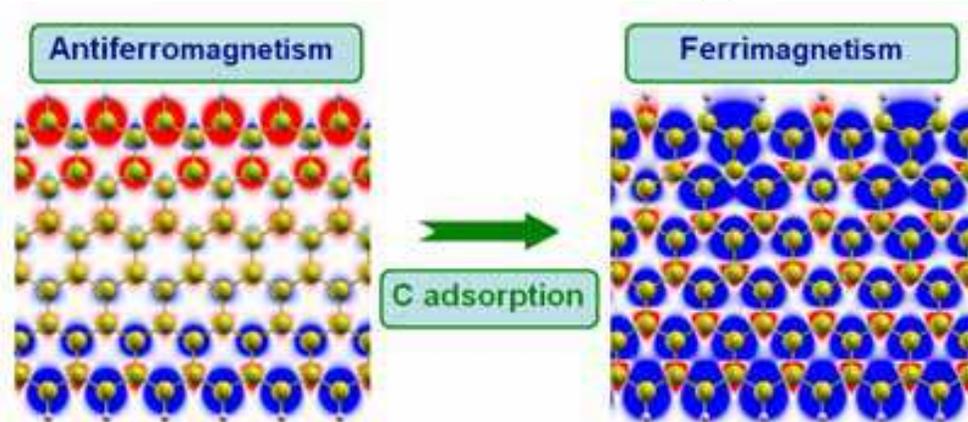


Fig. 18. Spin density of zigzag GNRs before and after adsorption. Red means spin-up density, while the blue means spin-down density (Kan et al, 2010).

Although they have answered the question whether adatoms can induce magnetic moments, there are still two critical questions: Whether do the magnetic moments survive with multi-adatoms? And whether all the zigzag GNRs have the same situations? To solve these questions, Kan et al. investigated the case with two adatoms. They found that two adatoms prefer the ferromagnetic coupling, and give a sum of induced magnetic moments of individual adatoms. By extending the studied model to other nanoribbons, they also found that all zigzag GNRs have the same results. Thus, their studies present an important way to manipulate the magnetism of zigzag GNRs.

#### 4. Experimental realizations of GNRs

Although theoretical works have proposed and predicted many interesting properties of GNRs, the experimental realizations of GNRs are still not easy. According to the fabricated methods, we can divide them into chemical and physical realizations. Normally, chemical methods are assembling the small molecules into GNRs, while physical methods are tailing the large graphene or nanotube into GNRs.

Many groups have reported the chemical fabrication of GNRs with small molecules. Yang et al. reported that the 1,4-diiodo-2,3,5,6-tetraphenylbenzene and 4-bromo-phenylboronic acid with other catalyst can produce GNRs with lengths of up to 12 nm (Yang et al, 2008). Recently, Cai et al. have reported atomically precise bottom-up fabrication of GNRs (Cai et al, 2010). In their research, they used surface-assisted coupling of molecular precursors into

linear polyphenylenes and their subsequent cyclodehydrogenation. Therefore, the topology, width and edge periphery of the GNRs products are defined by the structure of the precursor monomers, which can be designed to a wide range of different GNRs (Cai et al, 2010). However, accurate controlling the edge structures, width, and lengths of produced GNRs is still not easy for chemists.

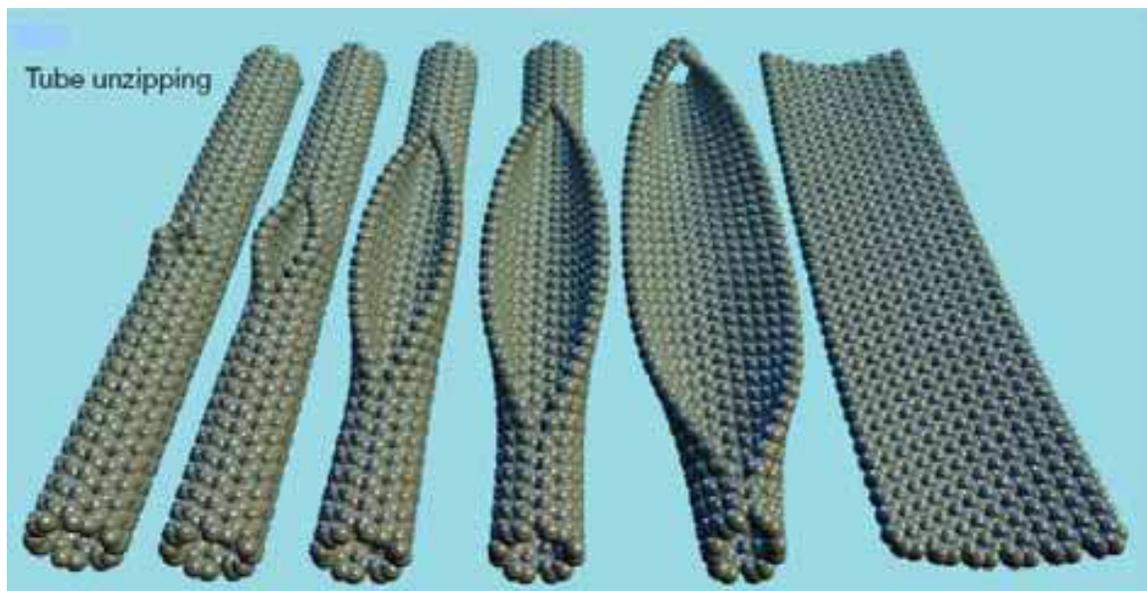


Fig. 19. Representation of the gradual unzipping of one wall of a carbon nanotube to form a nanoribbon (Kosynkin et al, 2009)

In this sense, cutting graphitic materials (Li et al, 2009) to form GNRs provides an alternative solution to partially overcome the obstacle. However, how to open the strong C-C bonding is a big challenge. As shown in Fig. 19, Kosynkin et al. have creatively proposed that using solution-based oxidative process to break the C-C bonds of carbon nanotubes. Their experimental results show a nearly 100% yield of nanoribbon structures (Kosynkin et al, 2009). On the other hand, Jiao et al. have proposed an approach to making GNRs by unzipping multiwalled carbon nanotubes by plasma etching of nanotubes partly embedded in a polymer film (Jiao et al, 2009), which is a completely physical method.

## 5. Summary

In this chapter, the geometric, electronic, and magnetic properties of GNRs are carefully discussed in both experiment and theory. Theoretical studies have shown that there are energy gaps in GNRs, due to the edge effects and quantum confinement effect. These results have well confirmed by experimental observations. However, the amazing magnetic property predicted in zigzag GNRs has never been observed in experiment. Several factors, such as carriers concentrations, edge structures, and thermal dynamic under limited temperature, are responsible for this situation. Thus, one very important question is how to make the magnetism more robust.

On the other hand, the experimental realization of GNRs are far away from the satisfaction. Since both edge structures, width, and length of GNRs are difficult to control, finding an effective way to overcome these problems becomes more and more important, both for academic research and industry applications.

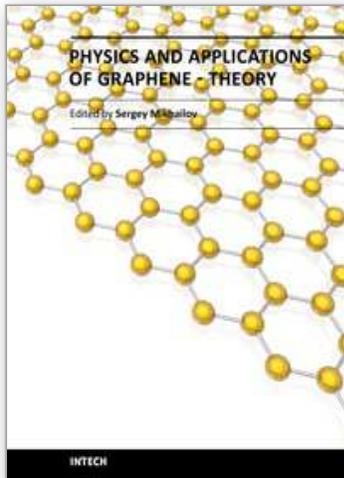
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## **Physics and Applications of Graphene - Theory**

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The Stone Age, the Bronze Age, the Iron Age... Every global epoch in the history of the mankind is characterized by materials used in it. In 2004 a new era in material science was opened: the era of graphene or, more generally, of two-dimensional materials. Graphene is the strongest and the most stretchable known material, it has the record thermal conductivity and the very high mobility of charge carriers. It demonstrates many interesting fundamental physical effects and promises a lot of applications, among which are conductive ink, terahertz transistors, ultrafast photodetectors and bendable touch screens. In 2010 Andre Geim and Konstantin Novoselov were awarded the Nobel Prize in Physics "for groundbreaking experiments regarding the two-dimensional material graphene". The two volumes *Physics and Applications of Graphene - Experiments* and *Physics and Applications of Graphene - Theory* contain a collection of research articles reporting on different aspects of experimental and theoretical studies of this new material.

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