Coupling effects of the electric field and bending on the electronic and magnetic properties of penta-graphene nanoribbons†

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Quasi one-dimensional materials made from carbon have attracted a lot of attention because of their interesting properties and potential applications in electronic devices. Recently, new kinds of carbon allotropes named as penta-graphene nanoribbons (P-GNRs) have been proposed. By implementing first-principles calculations, P-GNRs exhibit large tunable band gaps under bending stress, and the band gaps of P-GNRs are easier to control than those of GNRs. In addition, the order of spin moments of P-GNRs can transform from ferromagnetic to antiferromagnetic under the coupling effect of the electric field and bending strain, thus resulting in a significant change of magnetism. Therefore, the diverse electronic and magnetic properties highlight the potential applications of P-GNRs in flexible displays, wearable computation electronics and digital memory devices.

Introduction

Graphene has attracted considerable attention due to its excellent electronic and mechanical properties since its discovery in 2004. A pristine hexagonal graphene sheet is a gapless semiconductor, and the lack of a large tunable gap severely limit its application in electronic devices. However, the limitation can be overcome by cutting the 2-D sheet into quasi 1-D nanoribbons (GNRs). GNRs have larger band gaps, due to quantum confinement and spin splitting of the localized state. GNRs also have some other unique magnetic properties, for example, they are half-metallic. They are promising candidates for use in next generation field-effect transistors, spintronics, digital memory devices, flexible displays and wearable computation devices.

The electronic and magnetic properties of GNRs could be changed under bending. For example, Pan et al. reported a tunable band gap depending on the symmetries of edges and calculated the band gap of armchair GNRs under bending stress. For GNRs with a width of 16 (GNRs-16), the band gap increases firstly and then decreases as the bending stress is enhanced, while for GNRs with a width of 17 (GNRs-17), the band gap increases monotonously. The zigzag GNRs have been reported to transform from antiferromagnetic to nonmagnetic under large bending in previous studies. In addition, other types of mechanical deformations can also affect the electronic properties of graphene. For instance, Sun et al. studied the effects of uniaxial strain on the band gap of GNRs, and found that compressive strain can either narrow or widen the band gap depending on the width of the ribbon. Koskinen found that the band gap of armchair ribbons can be significantly widened or narrowed by planar bending where the bending load is dominated by compressive strain. Although GNRs have tunable electronic properties under external strain, the control range is sometimes not large enough for practical application. For example, when zigzag GNRs undergo a transition from an antiferromagnetic state to a nonmagnetic state, the change of magnetization is small and not easily detected. Consequently, GNRs have to be doped or form composites with transition elements like iron, cobalt or nickel for real applications.

So there is an urgent need to find a new kind of carbon material that has large tunable magnetism.

It is believed that carbon will act as a key material in the next generation of integrated circuits. Much attention has been paid to find new electronic materials from carbon allotropes. Recently, a new type of carbon allotrope called penta-graphene has been recently proposed, which can be exfoliated from T12-carbon. This new allotrope has two types of hybridization, sp² and sp³, which form pentagonal patterns resembling the Cairo pentagonal tiling. Recent research has revealed that this novel structure can also be obtained by implementing the chemical vapor deposition (CVD) method on a high index copper surface and the strength can be greatly enhanced by functionalization of hydrogen atoms. Unlike graphene, which is a zero

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bandgap semimetal, penta graphene has an intrinsic bandgap and has promising potential application in electronic devices. By cutting penta graphene along different crystallographic orientations, quasi-one-dimensional penta graphene nanoribbons (P-GNRs) can be obtained. P-GNRs show intrinsic magnetism because of the unpaired \( \text{sp}^2 \) hybridized electrons located at the edges. In addition, the band gaps of P-GNRs are larger than their parent sheet due to the quantum confinement effect.

Similar to GNRs, the band gaps of P-GNRs are also tunable under strain and the electric field. Rajbanshi et al.\textsuperscript{34} studied the changes in the band gap under uniaxial strain, and discovered that the band gap became smaller with increasing tensile strain. Yuan et al.\textsuperscript{35} proposed a method to tune the band gap with a transverse electric field. In addition, the band gaps of P-GNRs are also dependent on the width of nanoribbons. With increasing width, the band gaps of P-GNRs decrease marginally from 2.30 eV to 2.25 eV,\textsuperscript{34} while the band gaps of GNRs decrease from 1.50 eV to nearly zero.\textsuperscript{2,36} The stable band gap of P-GNRs holds promise for stable performance under harsh working conditions when it is integrated into a flexible display. Furthermore, P-GNRs have intrinsic magnetism and the energy bands split with different spins. So the valence band maximum (VBM) and the conduction band minimum (CBM) approach the Fermi level in different spin channels, and therefore P-GNRs can be used in bipolar magnetic semiconductors.\textsuperscript{35,37} P-GNRs show great advantages in both electric and magnetic fields.\textsuperscript{35,38} However, a systematic understanding of the electronic and magnetic properties of bending P-GNRs has not been established yet.

In this work, we present a detailed theoretical investigation on the electronic and magnetic properties of bending P-GNRs. By applying a vertical electric field and bending stress simultaneously, the magnetic configuration can be tuned from ferromagnetic to antiferromagnetic. This transition is useful once the ferromagnetic configuration is referred to as 1 and antiferromagnetic configuration is referred to as 0. Thus, each state can represent a logic bit, which is the basis of many memory devices. In addition, the band gap of bending P-GNRs can be linearly tuned from around 2.5 eV to nearly zero by applying an electric field. Because field effect transistors (FETs) with large tunable band gaps can be turned off effectively and have a large on/off ratio, P-GRNs are promising materials in this area. After bending, P-GNRs have significant charge separation due to elevated chemical potential and increased strain energy, and may open up potential applications in solar cells. The diverse electronic and magnetic properties of P-GNRs can be used to develop next generation digital memory devices and field transistors.

### Details of calculation

The simulations were based on the Dmol\textsuperscript{3} code. Using generalized gradient approximation (GGA) with Perdew–Burke–Ernzerhof (PBE) as the exchange correlation function.\textsuperscript{34,35,39} The basis was set to be double numeric plus polarization (DNP). The bending models of graphene nanoribbons were constructed by adjusting the positions of the atoms and the lattice parameter along the longitudinal direction. Then the structure was fully relaxed from the original model to reach the equilibrium state.\textsuperscript{21} The Brillouin zone is sampled by \( 1 \times 10 \times 1 \) \( k \)-points for all structures in the geometry optimization (electronic) calculations. The convergence tolerance was set with an energy of \( 1 \times 10^{-5} \) Ha, a maximum force of 0.002 Ha, and a maximum displacement of 0.0005 Å.\textsuperscript{2,39,40} A 20 Å vacuum was introduced between edges and layers to eliminate the interactions between nanoribbons.

### Results and discussion

To date, most methods of bending nanoribbons are reported for GNRs, but reports on bending P-GNRs are very rare. In previous studies, Hu et al.\textsuperscript{21} proposed a method by bending a flat ribbon into a sharp peak. However, the peak may cause too much deformation on P-GNRs and break the bonds since P-GNRs have three layers of atoms as shown in Fig. 1(a). Pan\textsuperscript{20} bent the ribbon into a smoother waved-like structure, but did not take into account the mismatches between the layers. Here, we propose a new method by bending the ribbons into a trigonometric function shape (Fig. 1(c)). A trigonometric function with its first

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**Fig. 1** Schematic of the nanoribbon model. The gray and white balls denote carbon atoms and hydrogen atoms, respectively. (a and b) The definition of the width of P-GNRs and GNRs. (c) The side views of GNRs and P-GNRs after bending into a trigonometric function shape. The bending strain \( \varepsilon \) is defined as \( \varepsilon = (c - c_0)/c_0 \). The arrow denotes the direction of the applied electric field.
Our obtained results are in good agreement with former studies. The band gaps of P-GNRs and GNRs with a specific width (w) are denoted as P-GNRs-w and GNRs-w, respectively. The degree of bending was characterized by strain ε = 1 − c/c0, where c0 and c denote the length of ribbons before and after bending (Fig. 1(c)). The atoms on the edges are saturated with hydrogen to avoid the influence of dangling bonds. To reduce the influence of planar strain, the new position of each atom is carefully arranged to make sure that the distances of atoms within the curved surface are the same as those in the flat plane.

Following the previous convention, the widths of ribbons (w) are defined as the rows across the ribbons as shown in Fig. 1a and b. P-GNRs and GNRs with a specific width (w) are divided into three categories according to their width, namely w = 3n, 3n + 1, and 3n + 2, where w is defined by the total number of C–C chains across the ribbon width and n is a positive integer. The variations of the band gap under bending are different from three categories of GNRs and are shown in Fig. S1, ESI†. With increasing bending strain, the band gap of the 3n category firstly decreases and then slightly increases, while the trend of band gaps of 3n + 1 is opposite. These band gaps first increase around 0.2 eV and then decrease. The band gap of the 3n + 2 category increases monotonously from 0.5 eV to around 1.5 eV. Our obtained results are in good agreement with former studies and confirm the accuracy of our calculation.

The structure of a penta-graphene nanosheet is shown in Fig. 2(a). By cutting a 2-D sheet along different crystallography directions, four types of P-GNRs with different edges are obtained, namely AA, ZA, ZZ, and SS. The SS type P-GNRs are obtained by cutting along the 45 degree angle direction with respect to the longitudinal directions of the pentagon. Because of the different cutting directions, all the double bonds of SS are arranged in a 45 degree angle with respect to the longitudinal directions, while the double bonds in ZZ, ZA, and AA have half of the double bonds arranged either parallel or perpendicular to the longitudinal direction. Since it is impossible to have arbitrary widths for fixed edge types of P-GNRs, the widths for AA, ZA, SS, and ZZ edges of P-GNRs are chosen to be 9, 8, 6, and 7. For simplicity, the structures in Fig. 2(b) are labeled as AA-9, ZA-8, SS-6, and ZZ-7. ZA, ZZ, and SS P-GNRs are more fragile than other types of P-GNRs. This fragility may be caused by the alignment of sp² bonds along the longitudinal direction. It has been known that double bonds have a planar configuration and thus can’t bend easily because of the coupling of the π bonding state. Since ZA, ZZ, and AA edges of P-GNRs have half of double bonds perpendicular to the longitudinal direction, only the double bonds aligned along the longitudinal direction will experience decoupling to some extent. However, all the double bonds of SS P-GNRs are arranged in a 45 degree angle with respect to the longitudinal direction, which will decouple

Fig. 2 (a) Schematic illustration of a penta graphene nanosheet. (b) AA-9, ZA-8, SS-6, and ZZ-7 P-GNRs obtained by cutting along different crystallography directions of the penta graphene nanosheet with different widths.
the π bonding state during bending and induce the fragility of P-GNRs.

The mechanical properties of P-GNRs during the bending process are studied by using strain energy $E_s$, which is defined as the total energy at a given strain $\varepsilon$ minus the total energy at zero strain. As has been proposed in ref. 20, the bending force was defined as in the following equation:

$$F_b = -\frac{\partial E_s(\varepsilon)}{\partial \varepsilon}$$

(1)

where $\varepsilon$ denotes the length of the nanoribbon. In order to obtain the bending force, a difference between two neighboring points on $E_s - \varepsilon$ data is calculated to approximate the true bending stress. When the bending strain is 5%, the corresponding bending forces ZZ-7, ZA-8, AA-9, and SS-6 are 2.56 eV Å$^{-1}$, 3.14 eV Å$^{-1}$, 3.71 eV Å$^{-1}$, and 2.19 eV Å$^{-1}$, respectively. While the bending force for armchair GNRs-7 is 1.4 eV Å$^{-1}$, which is significantly smaller than P-GNRs. Since P-GNRs have three atomic layers, it is reasonable that they are more rigid than GNRs, which has only one atomic layer. Furthermore, the inherent stiffness of P-GNRs has been verified by phonon dispersion analysis in Zhang’s work that the existence of the quadratic ZA mode in the long wavelength region manifests the bending stiffness.27

Secondly, P-GNRs exhibit richer magnetic properties than GNRs. There are three categories of magnetic configuration, (I) antiferromagnetically ordered spin at both edges, denoted as AFM, (II) ferromagnetically ordered spin along both edges, denoted as FM, (III) paramagnetically ordered spin along both edges, denoted as PM. All electronic and magnetic properties of the systems are firstly calculated in their ground states, which are identified by comparing the energies of AFM, FM and PM. The one with the lowest energy is the ground state. Since ZZ, ZA and AA edges of P-GNRs have intrinsic magnetism, and are found to have similar magnetic properties,25 we chose ZZ-7 P-GNRs as a specific example and present a detailed analysis of their magnetic properties. As for ZZ-7 P-GNRs, the theoretically calculated energies of AFM configuration are 26 meV and 111.5 meV lower than those of the FM and NM configurations.

Thus, the ground state of ZZ-7 P-GNRs should be AFM configuration. However, because the magnetic energy of P-GNRs far exceeds room temperature and the energy difference $(AE = E_{FM} - E_{AFM})$ is very small, FM configuration can also exist at room temperature,42 which is confirmed by the results obtained by Yuan.43 So all the initial magnetic configurations are set to be FM in the following studies.

The spin-polarized band structures of the ZZ-7 system are calculated to better understand the effects of bending strain, $\varepsilon$, on their electronic properties, which are shown in Fig. 4a–d. As shown in Fig. 4(a), without strain, the electronic distributions of the valence band maximum (VBM) and the conduction band minimum (CBM) approach the Fermi level, and are in different spin channels. The valence bands near the Fermi level show apparent asymmetry, indicating that the magnetism of the system is mostly determined by the valence bands. The density of state (DOS) and partial density of state (PDOS) show that the valence states near the Fermi level are mostly contributed by edge atoms, inferring that the edge atoms have a key role in determining the magnetic properties.

Moreover, in order to deeply describe the electronic structure of the ZZ-7 system, the corresponding spatial distributions of the highest occupied orbital (HOMO) and the lowest unoccupied orbital (LUMO) have been explored. The HOMO is comprised of only one spin and is also highly localized on the edge atoms, as shown in Fig. 4e. Furthermore, HOMO−1 and HOMO−2 (the first and second orbitals under HOMO), having only one spin, respectively, are also localized at the edge atoms (Fig. S2, ESI†). In addition, as shown in Fig. 4e, the spin charge distribution is also localized at the edge atoms, and the magnetism of ZZ-7 P-GNRs is contributed by the unpaired electrons on the edges. Therefore, it can be acknowledged that the edge atoms are important for determining the electronic and magnetic properties. With the bending strain increasing from 5% to 20%, Fig. 4b–d depicted the band structure of bending ZZ-7 P-GNRs. It is clear that the subband spacing and the energy gap of the deformed P-GNRs are tunable with bending strain. During bending, the conduction bands are shifted downward, thus the band gap decreases from 1.65 eV to 0.31 eV. As for the partial charge density distribution of energy bands near the Fermi level, the HOMO still remains at the edges, and therefore are HOMO−1, and HOMO−2 (Fig. S3, ESI†). However, the LUMO, which is primarily localized at edges without bending, migrates to the ridges of the bending ribbons after bending. Since this separation of hole and electron pairs, bending strain energy. Because the ridges exhibit a larger local curvature and bond stretching, the atoms at ridges have higher chemical energy potential. In addition, according to the Molecular Orbital (MO) theory, the chemical reactions are largely governed by HOMO–LUMO interactions. With the LUMO migrating to the ridges, we can conclude that the migration of the LUMO is...
related to the increase of strain energy and the chemical reactivity at the ridges is enhanced after bending. Meanwhile, the spins on edge atoms are also ferro-magnetically coupled, indicating that bending strain won’t change the magnetic configuration of the system.

For unbent P-GNRs, applying an electric field can’t tune the magnetic configuration. Therefore, bending the structure is a necessary condition to change the magnetic configurations. In order to tune the magnetic properties of P-GNRs, we propose a method by first bending the nanoribbon, and then applying a vertical electric field ($E$). Taking ZZ-7 P-GNRs with a 10% bending strain as an example, the magnetic configurations will change from FM to AFM and finally to PM with the increase in the electric field from 0.0 V Å$^{-1}$ to 0.8 V Å$^{-1}$, which are depicted in Fig. 5e. To further explore the transformation of magnetic configuration, the band structure, density of state and charge Fig. 4 (a–d) Band structures and density of states for P-GNRs under bending strains of 0%, 10%, 15%, and 20%, respectively. The Fermi level is set to zero. Black and red lines denote spin up and spin down energy bands. The dash blue line denotes the contribution of carbon atoms at the edges to the total density of states. (e) Charge densities of the HOMO and the LUMO. Blue and yellow circles denote the positive and negative wave function at the Gama point, and the isosurface value is set to $\pm 0.02$ e Å$^{-3}$. Spin density distribution is defined as $\Delta \rho = \rho_{\text{up}} - \rho_{\text{down}}$. Pink and cyan circles correspond to the isosurfaces of up (positive) spin density. The isosurfaces are set to $\pm 0.022$ e Å$^{-3}$. Since all the spins are spin up, there is no cyan color for the isosurfaces in the SPIN diagram.
distribution are analyzed. As shown in Fig. 5a, when the electric field is equal to zero, edge atoms have all the spins aligned in the parallel direction, therefore the structure has FM configuration and the total magnetic moments reach the maximum value of $8 \mu_B$. With the increase of the electric field to $0.25 \text{ V } \text{Å}^{-1}$, the conduction bands of both spins are shifted downward and the band gap decreases from $1.41 \text{ eV}$ to $0.8 \text{ eV}$. When the electric field reaches up to $0.43 \text{ V } \text{Å}^{-1}$, which is a critical value for magnetic configuration transition, the valence band of down spin is shifted upward, causing energy bands of opposite spins to degenerate and the total magnetic moments drop to $0 \mu_B$. Upon further increasing the strength of the electric field, the bands of spin-up keep shifting downward, while the bands of down spin change only marginally. Until the energies of spin-down became higher than spin-up, the structure has net magnetic moments again and transforms into paramagnetic configuration. The total magnetic moments of PM configuration could be between those of FM and AFM configurations. In this way, an atomic “bit” could be obtained by superimposing an electric field, once the FM and AFM states are referred to as “1” and “0”.44,45 Since the electric field can be easily controlled with high precision, it provides a convenient method to tune the magnetic configuration of bending P-GNRs.

By implementing a dichotomy method near the electric field, where the flip of the spin occurred, a critical electric field strength as a function of bending strain could be summarized.
in Fig. 6 to get an overall picture of the magnetic transitions for different bending P-GNRs. The critical electric fields for the magnetic configuration transition from FM to AFM decrease gradually with increasing bending stresses. This means that the electric field and bending stress work cooperatively to tune the magnetic transition of P-GNRs. In addition, when either the electric field or bending strain is large enough, another magnetic configuration transition from AFM to PM could occur. The changes in the total magnetic moments in the FM–AFM transition are much larger than those in the AFM-PM transition. The FM–AFM magnetic transition indicates that the ‘1’ and ‘0’ states are more distinguishable and are more useful in digital memory devices. Furthermore, as shown in Fig. 6, when 0.08 < \(\varepsilon\) < 0.11, the AFM region is relatively small, suggesting that the tuning range of the electric field is small. However, when \(\varepsilon\) < 0.08 or \(\varepsilon\) > 0.11, the AFM region is larger. Thus, slightly strained or severely strained P-GNRs and their coupling with the electric field are more effective in tuning the magnetic properties than moderate strained P-GNRs as applied in memory devices.

In order to obtain a better understanding of the band gaps under the electric field, ZZ-7 is selected as a specific example, and the bending strain is set to 5%, 10%, 15% and 20%. Fig. 7 shows that the band gaps of bent P-GNRs decrease almost linearly with increasing electric field. However, at a certain strength of the electric field, the band gaps suddenly increase around 0.05 eV and then continue to decrease linearly. These sudden jumping points are accompanied by the transition of magnetic configuration and correspond to the critical electric field for the FM–AFM transition. When the electric field becomes very large, all the band gaps become very close to zero. In addition, the curves of larger bending strain have steeper slopes, indicating that the band gaps of bent P-GNRs are more sensitive to the external electric field. After bending, the LUMO separates from the HOMO by migrating from the edges to the center of the ridges. Due to the coupling effect of an electric field, the LUMO and the HOMO will have different electrostatic potential energies and thus lower and higher energies of conduction bands and valence bands. So the decrease of the energy band gap is determined by the electrostatic potential difference. Since large bending strain will increase the distance between the LUMO and the HOMO, and the electrostatic potential difference will also become larger, the band gaps of P-GNRs under larger bending strain will drop more quickly with the electric field. Thus, the changes in the electrostatic potential need to be calculated. Here we approximate the electrostatic potential by \(E\varepsilon - c_0\), where \(E\) is the strength of the electric field, \(\varepsilon\) is the bending strain, and \(c_0\) is the length of a nanoribbon. The band gap was plotted as a function of electrostatic potential in the inset of Fig. 7, and the slopes of the curves are similar. These results approve that the changes of the band gap are caused by the electrostatic potential difference under different electric fields.

**Conclusion**

In summary, we have found that the electronic and magnetic properties of P-GNRs are sensitive to the electric field and bending stress. The band gaps of P-GNRs decrease monotonously with bending strain while the band gap of GNRs can either decrease or increase depending on the width. P-GNRs have intrinsic ferromagnetism which can be tuned into antiferromagnetism under a cooperative effect of bending strain and the electric field. This magnetic transformation is useful in digital memory devices. In addition, bending strain can cause the separation of the LUMO and the HOMO of P-GNRs, which can be promising materials for solar cells. The band gaps of bent P-GNRs are also tunable by a vertical electric field due to the electrostatic potential. Our calculation provides a simple method to manipulate the electronic and magnetic properties of P-GNRs, which are helpful for the design of novel transistors and photovoltaic devices.
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