Switchable metal-to-half-metal transition at the semi-hydrogenated graphene/ferroelectric interface†

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Tuning the half-metallicity of low-dimensional materials using an electric field is particularly appealing for spintronic applications but typically requires an ultra-high field, hampering practical applications. Interface engineering has been suggested as an alternative practical means to overcome this limitation and control the metal-to-half-metal transition. Here, we show from first-principles calculations that the polarization switching at the interface of semi-hydrogenated graphene (i.e., graphone) and a ferroelectric PbTiO3 layer can reversibly tune a metal to half-metal transition in graphene. Using a simple Hubbard model, this is rationalized using interface atomic orbital hybridization, which also reveals the origin of the high-quality screening of metallic graphone, preserving bulk-like stable ferroelectric polarization in the PbTiO3 film down to a thickness of two unit cells. These findings do not only open a new perspective on engineering half-metallicity at the interface of two-dimensional materials and ferroelectrics, but also identify graphone as a powerful atomically thin electrode, which holds great promise for the design of ultrafast and high integration density information-storage devices.

1. Introduction

The specific properties of half-metallic materials, such as 100% spin polarization current in one spin channel, make them ideal candidates for spintronics applications.1 Accordingly, engineering half-metallicity in various materials, particularly in low dimensional materials, has become a popular subject of both theoretical and experimental interest over the past years.2–11 Graphene is considered as a promising spintronics material associated with a long spin-relaxation time at room temperature and weak spin–orbit coupling.12–14 However, graphene is intrinsically a non-magnetic semi-metal with zero band gap and it is therefore necessary to modify its electronic structure through an external stimulus to make it half-metallic.

Many strategies have been explored to achieve and potentially control half-metallicity in graphene and related compounds, including chemical modification,15–23 and application of electric fields24–29 and elastic strains.30,31 Amongst them, the application of an electric field has long been considered as an effective way to tune half-metallicity, especially in one-dimensional (1D) zigzag graphene nanoribbons.3,24–27 More recently, it has been theoretically demonstrated that an electric field can even induce half-metallicity in 1D carbon nanotubes.28,29 Typically, a transverse electric field is applied so that the edge-state electrons can be transferred from one side to the other side of the system, making it half-metallic. However, from theoretical predictions, rather high electric fields are typically required to achieve half-metallicity. This makes the practical realization of the concept very challenging2,25 and asks for alternative approaches to induce and control the half-metallicity in graphene.

Owing to the recent breakthroughs in fabricating high-quality graphene–ferroelectric (FE) heterostructures,32–39 exploitation of proximity effects using FE polarization, which can be conveniently controlled by electric fields, opens up potential new perspectives to engineer half-metallicity in graphene. Polarization has already been demonstrated to effectively modulate the electronic structure and carrier density of graphene-based compounds. Zheng et al. successfully realized the switching between the high- and low-resistance states of...
graphene by controlling the polarization of the FE thin film in a graphene–FE hybrid device. Kim et al. found that the hole density in graphene could be tuned by reversing the polarization of the FE polymer layer. Baumer et al. suggested that both the carrier type and the density of graphene could be altered by the polarization of the PbZr0.2Ti0.8O3 layer. Based on such great successes, it can be expected that half-metallicity maybe realized by properly tuning the FE polarization but, to the best of our knowledge, no such a realization has been reported yet.

Here, considering a graphene nanosheet with semi-hydrogenation along the zigzag direction deposited on top of a FE PbTiO3 (PTO) thin film as a prototypical system, we show that half-metallicity can be switched on and off in the graphene layer by the reversal of polarization in the PTO thin film, a phenomenon explaining by the formation of an interfacial C–O bond and charge transfer. Our Hubbard model reveals that transferred charges due to covalent bonding at the interface screen a significant amount of surface charges, preserving bulk-like ferroelectricity down to a thickness of less than 10 Å. It is further suggested that such a screening effect is general and also relevant to other chemically modified two-dimensional (2D) materials like graphene partly-doped by hydrogen atoms, making atomically-thin 2D materials promising to replace traditional metal and oxide electrodes to efficiently screen the depolarizing field. These findings may both stimulate experimental investigations and provide useful guidance for future applications in graphene-based devices.

2. Computational details

Calculations are performed in the framework of density functional theory (DFT), using the projector-augmented wave (PAW) method as implemented in VASP. The exchange–correlation energy is described using the generalized gradient approximation (GGA) of Perdew–Burke–Ernzerhof, which is widely used for studying the half-metallicity of graphene. An on-site Coulomb energy $U = 3$ eV is applied to Ti d orbitals. Although GGA is known to overestimate FE polarization, with the $U$ correction it yields a reasonable value of 0.94 C cm$^{-2}$ in bulk PTO. A plane-wave cutoff energy of 500 eV and a $5 \times 9 \times 1$ Monkhorst–Pack $k$-point mesh are used to accurately describe the electronic properties. During the structural optimizations, the lattice parameters are kept constant, while the internal coordinates of the atoms are fully relaxed until the Hellmann–Feynman force on each atom is lower than 0.01 eV Å$^{-1}$. The phonon dispersion is calculated using the density functional perturbation theory (DFPT) method. A Hubbard model, which includes hopping kinetic energy ($t$) and on-site Coulomb repulsion ($U$) is represented by:

$$H = -t \sum_{\langle \sigma \rangle} \sum_{\alpha} \epsilon_{\alpha, \sigma} c_{\alpha, \sigma}^\dagger c_{\alpha, \sigma} + \text{C.C.} + \sum_{\alpha} \epsilon_{\alpha} n_{\alpha, \sigma} + U \sum_i n_i \sigma n_i \sigma. \quad (1)$$

Fig. 1 (a) Charge density of the $p_z$ orbital in graphene and (b) phonon dispersion of graphene, (c) side view and (d) top view of graphene/(PbO–TiO$_2$)$_m$ PbO/graphene heterostructures.
zigzag chain of hydrogen adsorbed on half of the carbon atoms. In such a case, the 2D π-network of graphene is broken and the remaining π, orbitals reform a 1D π-bonding chain parallel to the hydrogen chain and dominate the states around the Fermi level. The zigzag-type graphene exhibits metallic and nonmagnetic properties in its free-standing form, which is structurally and physically different from the semiconducting and ferromagnetic chair-type graphene used in ref. 47–49, and the insulating and nonmagnetic boat-type graphene used in ref. 50. Detailed symmetry analysis using FINDSYM showed that the space group changes from hexagonal P6/mmm to orthorhombic Pma2 after semi-hydrogenation.51,52 A similar functionalization scheme was recently used in studies to induce edge states in carbon nanotubes.53

To examine the dynamical stability of zigzag-type graphene, phonon dispersion curves were calculated. As shown in Fig. 1(b), no unstable mode is found, attesting that zigzag-type graphene is dynamically stable, which makes it possible to synthesize in experiments through e.g. hydrogen plasma,54,55 wet chemical approach,56,57 and scanning tunneling microscopy methods.58 The other two types of semi-hydrogenated graphene are excluded here to investigate the half-metallic property. Although the stability of chair-type graphene was supported both by molecular dynamics simulations57 and its negative binding energy,58 indicating it can be synthesized, it was proposed recently that boat and zigzag types of graphene have much lower energy than chair-type graphene.50 Therefore, they should be relatively easier to synthesize in experiments. In terms of boat-type graphene, each two undoped carbon atoms form a dimer isolated from the other undoped carbon atoms and without interactions. After forming a bond with interfacial oxygen atoms of PTO, such a zero-dimensional C–C–O system remains isolated and insulating due to the confinement of the electron wavefunction.50

3.2. Ferroelectricity controlled metal–half-metal transition

To achieve control of the electronic properties of graphene thanks to the polarization at the graphene/PTO interface, we first need to verify that graphene provides enough screening for the spontaneous polarization to be preserved in the PTO thin films. Polarization is indeed known to be suppressed in FE thin films depending on the screening provided by the electrodes.59 Electrodes such as Fe, Pt, SrRuO3 and 2D boat-type graphene had already been demonstrated to effectively screen the surface charges and stabilize the polarization.50,59–64 Identifying the critical thickness for ferroelectricity in the presence of a zigzag-type graphene electrode is not only important to determine the minimum size of a realistic simulation stack but also to establish the eventual scaling-down limitation of related practical devices.

Fig. 1(c) and (d) provide side and top views of the simulated PTO layer (for \( m = 2 \)) sandwiched between metallic graphene layers. To explore the stability of the FE phase of the heterostructures, \( m (m = 2, 4, 6 \) and 8) layers of PTO with an initial polar distortion are fully relaxed to determine the ground state configuration. Four different spin configurations are explicitly considered: non-magnetic (NM), ferromagnetic (FM), antiferromagnetic (AFM) and ferrimagnetic (FIM) configurations.

Firstly, the energy of the FIM state at all PTO thicknesses is lower than that of the NM state, and the initial FM and AFM states converge to the FIM state after optimization. Secondly, Fig. 2(a) displays the differences of energy between the FIM-FE and NM-FE states and the NM-paraelectric (PE) reference. It is clear that the FE state is always the ground state. The energy difference between the NM-FE and FIM-FE states remains nearly constant with \( m \), attesting that the magnetization is mainly located in the graphene layer, which will be further explained in the next section. More interesting, a net polarization remains at a PTO thickness of two unit cells and the energy difference between the NM-FE and NM-PE states increases almost linearly with \( m \), highlighting a thickness independent \( \Delta E = (\text{FE} - \text{PE})/m \). This point suggests that the polarization remains nearly independent of the PTO thickness, which is further supported by the atomic rumpling: in Fig. 2(b), we see that the Ti–O and the Pb–O rumpplings in the internal PTO layers keep almost constant at all thicknesses. According to previous works,50,59–64 incomplete screening of the depolarizing field should result in a progressive suppression of ferroelectricity when reducing the thickness; the current result indicates that the depolarizing field maybe almost completely screened at the graphene/PTO heterostructures. This is further confirmed by the macroscopic average of the planar electrostatic potential along (001) direc-

![Fig. 2](image-url)
tion for PTO slab and graphene/PTO heterostructures \((m = 4)\) as shown in Fig. S1.†

After demonstrating that polarization can be preserved in ultrathin PTO films covered by graphene, our next goal is to determine whether polarization affects the electronic properties of graphene. Fig. 2(c) shows the density of states (DOS) of the graphene layer with inward and outward polarizations of a PTO layer with a thickness of two unit cells. It should be noted that the Fermi level of graphene lies right in the band gap of PTO, which prohibits the spill-out of charge from graphene.65 The results highlight that even though graphene remains NM and metallic for inward polarization (finite DOS at the Fermi level for up and down spins), it becomes half-metallic through polarization switching. This demonstrates the possibility to trigger a metal-to-half-metal transition at the graphene/FE interface, making graphene a promising material for spintronics devices in the future. The results remain unchanged for graphene sheets on top of a PTO layer whose thickness is varied up to 8 unit cells (see Fig. S2†). This indicates that the transition arises from the interfacial graphene/FE interactions and that the half-metallic state is a general characteristic of graphene when the polarization is outward.

3.3. Interface interaction and origin of half-metallicity

To understand the emergence of spin polarization and half-metallicity, we developed a minimal Hubbard model that gives direct access to the C–O hybridization at the interface, and the Coulomb repulsion included is important for the exchange interactions and magnetic property of graphene. The geometric structure of the model is shown in Fig. 3(a). Only the electronic bands near the Fermi energy are included in the model, namely, the \(p_z\) orbitals of the C atoms that are not bonded to H atoms. The \(p_z\) orbitals of O atoms linked with the C chain are considered so that we can simulate the effect of the C–O hybridization. The kinetic energies of the hopping electrons of C–C and C–O are set to \(t\) and \(t_{CO}\), respectively. We only added the potential energy of on-site Coulomb repulsion \(U = 2.5t\) to the C \(p_z\) electrons while the on-site potential energy of \(\varepsilon_C\) and \(\varepsilon_O\) are set to be 0 and \(-0.5t\). The Hartree–Fock approximation is used to solve the Hubbard model.

Since O atoms could gain electrons both from Pb and C, it is difficult to precisely quantify the number of electrons that should be included in the Hubbard model. We suggest that whether or not the electronic structure of the DFT results can be well reproduced is an effective test to determine the amount of electrons. A series of calculations are performed by gradually changing the total electrons from 6 (\(0^+\)) to 10 (\(0^+\)). Comparing the DOS for C atoms from C1 to C4 with that of results from the DFT calculations, we confirm that the main features (e.g., spin splitting, positions of peak and Fermi energy, etc.) fit very well with 8.2 electrons (see details in Fig. S3†). Thus, 8.2 electrons will be used in the model in the following.

To identify the interfacial interactions, of particular interest is the evolution of the electronic structure as a function of \(t_{CO}\), which reflects the strength of the interfacial interactions. Fig. 3(b) shows the evolution of the DOS at fixed amplitudes of \(t_{CO}\). When \(t_{CO}\) is equal to zero, there are no interfacial interactions and the graphene layer remains in the same NM metallic state as the graphene 2D sheet. As \(t_{CO}\) gradually increases, there is a split between the C–O hybridized anti-bonding and bonding states, which breaks the C–C chain and makes the C \(p_z\) electrons more and more localized. As a result, the 1D \(\pi\)-bonding chain is broken and a barrier splits the C–C chain into a single C atom (C1 in Fig. 3(a)) and a triple C chain (C3–C4–C5).

For atom C1, the orbitals are about half filled; therefore, the on-site Coulomb interaction leads to spin polarization. For the remaining three-atoms chain, the magnetic properties are \textit{a priori} more complicated. Assuming the barrier is large enough and this chain can be isolated from the rest of the system, some insight can nevertheless be gained from simple analysis of it. Taking into consideration only the nearest-neighbor hopping electrons with kinetic energy \(t\), the system has eigenenergies (\(-\sqrt{2t/2}, 0, \sqrt{2t/2}\)). The lowest energy band is doubly occupied and has no spin polarization. The state with zero energy, which has an eigenvector \(\sqrt{2} (\psi_1 - \psi_2) / 2\), is occupied by one electron and has no \(\psi_2\) component. The onsite electron–electron interaction leads to a spin splitting. Thus, the magnetic moments of atoms C3 and C5 are parallel and are both equal to around 0.5\(\mu_B\) when the Mott gap is open, whereas atom C4 has no spin polarization. Owing to the non-zero hybridization between the \(p_z\) orbital in the triple C chain and the other C atoms, the magnetization of the triple C chain is slightly different from (0.5, 0, 0.5)\(\mu_B\), resulting in the FIM state with (0.46, −0.19, 0.46)\(\mu_B\) when \(t_{CO}\) = 1.2t. This unusual FIM
behavior is further confirmed by the spin charge density obtained from first-principles calculations, as shown in Fig. 3(c). A magnified figure of the spin density is plotted in Fig. S4† to clearly show the spin polarization of interfacial O atoms and the interfacial C–O bond. Owing to the formation of a covalent bond between the nearest two C₂ and O atoms, the C₁ atom becomes unpaired and the localized electrons result in spontaneous magnetization. For the other three carbons, namely C₃, C₄, and C₅, we found that the positive spin density is localized mainly on C₃ and C₅, while C₄ carries a smaller negative spin density. The values of magnetization of C₁, C₃, and C₅ as a function of tₓₒ are represented in Fig. 3(d). The magnetic moments obtained from the Hubbard model with tₓₒ = 1.2t show good agreement with the values obtained by first-principles calculations (dash lines), further confirming the reliability of the Hubbard model. Similar FIM behavior was observed in earlier studies of half-filled graphene,⁶⁶ graphene with chemisorbed hydrogen⁶⁹ and defect graphene.⁶⁷

The interfacial interaction is also supported by crystal orbital overlap population (COOP)⁶⁸ analysis of the results. From the above discussions, the main effect of the PTO layers on the electronic properties of graphene is the formation of interfacial C–O bonds, which is accompanied by charge transfer from C to more electronegative O. Additionally, the electrons of graphene also contribute to further screening the surface charge of the FE layer. To verify qualitatively the presence of charge transfer, we have performed Bader charge analysis for FE and PE states of the heterostructures (with and without interaction between graphene and PTO).⁶⁸ The results confirm that the graphene layer lost electrons by around 0.83e. Such a reduction of the number of electrons in metallic graphene affects the strength of spin splitting and the position of Fermi energy, which in turn induces the metal–half-metal transition.

To explore how the number of electrons affects the electronic structure of graphene and so check our hypothesis, we plot in Fig. 4(a) the DOS associated with our Hubbard model as a function of the total number of electrons included in the model. It appears that the position of the Fermi energy is progressively decreased with the reduction in the number of electrons. More interestingly, only the down-spin electrons cross the Fermi energy and become progressively unoccupied, which significantly enhances the spin splitting and gives rise to the half-metallic state with fractional charge transfer. Therefore, it is reasonable to conclude that the charge transfer which directly alters the occupied spin-down electrons triggers the transition to the half-metal state.

3.4. Insight into the screening properties of 2D materials

Finally, we would like to gain further insight into the exceptional screening properties of zigzag-type graphene, which are essential for preserving the FE polarization and achieving control of the metal–half-metal transition. For comparison, we also investigate here the screening properties of pure graphene, duplicating our calculations for graphene/PTO heterostructures with PTO thicknesses from 2 to 8 unit cells. Surprisingly, although graphene has electronic states at the Fermi level, the polarization is completely suppressed even at 8 unit cells of PTO, revealing the critical role of semi-hydrogenation on the screening properties. The bad screening properties are further confirmed by the large fields appearing when forcing the PTO polarization and can be related to distinct effects: (i) comparison of the lowest-frequency phonon mode related to out-of-plane displacement of carbon atoms for graphene (468 cm⁻¹) and graphene (114 cm⁻¹) indicates that the 2D π-network of graphene is much stronger than the 1D π-line of graphene, so that the interaction with FE PTO cannot break the symmetry and there is no strong interaction at the interface, (ii) all the carbon atoms are in the same plane in graphene, while graphene adopts a low-symmetry bucked structure in which undoped carbon atoms are closer to the interfacial oxygen atoms, resulting in the strong C–O bonding and better screening properties of graphene. Previous works, combining experiments and DFT calculations, revealed that electronegative (OH, O, HCOO) and electropositive (H, HCO) adsorbates are much more effective than conventional metal electrodes in stabilizing ferroelectricity.⁷⁰,⁷¹ Once the 1D π-bonding chain of graphene is broken, the behaviors of carbon atoms with one unpaired electron are similar to electropositive adsorbate on the surface of PTO, which may screen a significant amount of surface charge.

To disentangled further the pure interfacial effects from electrostatic effects,⁷² we modified the previous Hubbard model including now only the two graphene layers with and without C–O bonding (tₓₒ = 1.2t and tₓₒ = 0, respectively) and four interfacial oxygen atoms. Since there is no polarization, the charge transfer mechanism to neutralize the polarization charge is excluded. The difference in electrons between the

![Graph showing the density of states](image-url)
two graphene layers is shown in Fig. 4(b). By studying this system with a tunable number of electrons, we found that there is a large electron transfer from the C–O bonded layer to the C–O unbonded layer, which effectively screens the depolarization field and reduces the electron number in the C–O bonded graphene layer. Therefore, the better screening effect of graphene compared with traditional metallic electrodes originates from the fact that graphene not only provides electrons to screen the bond charges like metal but also acts as an electropositive adsorbate which provides more effective charge screening. The importance of a detailed microscopic analysis of screening effects was stressed by Stengel et al. who demonstrated that the stretching effect due to the bond between electrode and oxygen can stabilize FE polarization. Here we show that the charge transfer between electrodes caused by covalency provides another possibility for highly effective screening.

The exceptional screening properties of graphene make it a valuable alternative to thicker conventional electrodes for the realization of ultimately thin FE capacitors and leads to new opportunities towards miniaturization of ultrahigh-density devices. Although semi-hydrogenated graphene has not been synthesized yet experimentally, partially hydrogenated graphene has already been realized by hydrogen plasma and wet chemical approaches. More recently, fine control of adsorption was reported and chemisorption of a single H atom on graphene was realized in scanning tunneling microscopy experiments. To further assess the generic character of our findings, we replaced graphene by graphene adsorbed by one H atom per PTO unit cell area, and found that it can similarly stabilize the polarization of PTO down to two unit cells (see Fig. S5†). Therefore, it can be expected that the covalent bonding mechanism enhanced screening effect may be extended to other chemically modified 2D materials: if the electrode can provide unpaired electrons, it may also be efficient in stabilizing polarization. It should be noted that the ferroelectricity, electronic structure and interfacial interactions may be highly sensitive to the electrical boundary conditions. The specific interface between graphene and alternative systems of ferroelectric films on a substrate without or with a conventional bottom electrode may have new physics such as polarization controlled resistance and conductivity, which will be our research target in the future.

4. Conclusions

In summary, a new approach to trigger reversibly metal–half-metal transition in semi-hydrogenated graphene at its interface with a ferroelectric material is reported. Through first-principles calculations, we demonstrate that metallic graphene is dynamically stable and can effectively screen the depolarization field in order to stabilize a sizable polarization in a ferroelectric film with a thickness as small as two unit cells. Furthermore, we found that metallic graphene becomes half-metallic under polarization reversal. An in-depth analysis based on a simple Hubbard model provides clear evidence that the half-metallicity originates from the strong hybridization between interfacial carbon and oxygen atoms and electron redistribution in graphene. Such strong hybridizations are further shown to be the origin of the good screening effect of graphene. Our findings are quite general and open new perspectives for the design of half-metallic two-dimensional materials and high-density ferroelectric devices. On the one hand, the mechanism of inducing half-metallicity in graphene can easily be applied to other ferroelectrics since only interfacial interactions and charge transfer are needed. On the other hand, it can be expected that, similarly to graphene, other chemically modified two-dimensional materials with unpaired electrons may also hold great promise to replace traditional “thick” metal or oxide electrodes. In light of the advances in the synthesis of two-dimensional material/ferroelectrics heterostructures, we hope our findings will fuel further experimental works on their interfacial properties.

Conflicts of interest

There are no conflicts to declare.

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