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**The Two-Dimensional MnO₂/Graphene Interface: Half-metallicity
and Quantum Anomalous Hall State**

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ABSTRACT

We explore the electronic properties of the MnO₂/graphene interface by first-principles calculations, showing that MnO₂ becomes half-metallic. MnO₂ in the MnO₂/graphene/MnO₂ system provides time-reversal and inversion symmetry breaking. Spin splitting by proximity occurs at the Dirac points and a topologically nontrivial band gap is opened, enabling a quantum anomalous Hall state. The half-metallicity, spin splitting, and size of the band gap depend on the interfacial interaction, which can be tuned by strain engineering.

1. INTRODUCTION

Exfoliation of graphene has triggered the exploration of the class of two-dimensional (2D) materials.¹ Many new 2D systems have been fabricated, such as boron nitride, transition metal dichalcogenides, and early transition metal carbides/carbonitrides.²⁻⁷ These materials exhibit physical and chemical properties distinctly different from their bulk counterparts. Particularly, they potentially provide flexibility, low weight, and dramatically reduced device sizes, thus being considered as key to future applications in nanoelectronics, optoelectronics, energy conversion, and energy storage.⁸⁻¹⁴ With the research on basic properties of 2D materials probably having passed its zenith, the focus nowadays is shifting to applications.¹⁵ It has been demonstrated that the integration of 2D materials into vertical van der Waals heterostructures is a powerful strategy to leverage and combine the features of different 2D components.¹³⁻²¹ Such hybrid systems preserve well individual intrinsic material properties due to the absence of strong chemical bonding, while interfacial charge transfer and coupling have the potential to yield novel functionalities.²²⁻²⁶

Introduction of spin polarization is a prerequisite for realizing graphene-based spintronics, a field of intense present interest.²⁷⁻²⁹ The deposition of adatoms has been considered^{30,31} but is probably not a feasible strategy, because often cluster formation cannot be avoided.^{32,33} Since magnetic metallic substrates would lead to short circuits,³⁴⁻³⁷ attention has been drawn to the coupling of graphene to magnetic insulators.³⁸⁻⁴³ However, 2D materials are rarely considered for exploiting the proximity effect, due to a limited availability of monolayer systems with intrinsic magnetism,⁴⁴ though this approach could facilitate all-2D graphene-based spintronics. The magnetic material itself also can be significantly affected by

the contact to graphene as its electronic structure may be modified, potentially yielding novel functionalities.²²

Monolayer manganese dioxide (MnO_2) is predicted to be a ferromagnetic semiconductor with high Curie temperature.⁴⁴ Recently, it has been shown experimentally that a low Mn vacancy concentration induces half-metallicity,⁴⁵ reflecting a high susceptibility to external stimuli. Thus, monolayer MnO_2 is an ideal material to explore the interaction with graphene. Though the MnO_2 /graphene hybrid system has been realized experimentally and subsequently has drawn extensive attention in electrochemical applications,⁴⁶⁻⁵⁰ an analysis of its electronic structure from a theoretical point of view is still lacking. For this reason we present in the following detailed results from first-principles calculations, which provide important insights in the material properties. In particular, we demonstrate that the interfacial coupling induces half-metallicity in MnO_2 and that the magnetic proximity enables a quantum anomalous Hall state in graphene.

2. COMPUTATIONAL METHODS

First-principles calculations are performed using the Vienna Ab-Initio Simulation Package with the spin-polarized Perdew-Burke-Ernzerhof exchange correlation functional. In order to model strong electronic correlations in the localized Mn $3d$ orbitals, we include an on-site Coulomb interaction with effective parameter $U - J = 3.9$ eV,^{51,52} Though this approach is limited with respect to the anisotropic Coulomb interaction,^{53,54} our results on the magnetism of monolayer MnO_2 agree well with those based on the Heyd-Scuseria-Ernzerhof exchange correlation functional.⁴⁴ A cutoff energy of 500 eV and a $30 \times 30 \times 1$ k-mesh are used. The

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4 geometry is optimized until all residual forces are less than 0.01 eV/Å. In each configuration
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6 the length of the supercell along the *c*-axis is chosen to be 40 Å, resulting in a vacuum layer
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8 of at least 28 Å thickness. Due to the reduced chemical bonding, a damped van der Waals
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10 correction (D2) is employed to model nonbonding forces.^{55,56}
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16 3. RESULTS AND DISCUSSION

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18 The relaxed lattice constants of individual graphene and MnO₂ monolayers turn out to be
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20 2.469 Å and 2.926 Å, respectively, agreeing well with previous results.^{44,57} Therefore, we
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22 built a commensurate lattice with $\sqrt{3} \times \sqrt{3}$ and 2×2 periodicity, respectively, for MnO₂ and
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24 graphene, which results in 2.6% lattice mismatch. There exist three possible stacking patterns,
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26 as shown in Figs. 1a-c: The O^{2nd}, O^{1st}, and Mn centered configuration, respectively, has an
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28 atom from the lower O layer, upper O layer, and Mn layer on top of the hollow site of
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30 graphene. The average value of the MnO₂ and graphene lattice constants is adopted and kept
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32 fixed in the MnO₂/graphene and graphene/MnO₂/graphene systems. The interfacial binding
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34 energy is defined as $E_B = E_{HS} - E_M - E_G$, where E_{HS} , E_M , and E_G are the total energies of the
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36 hybrid system, individual MnO₂ monolayer, and graphene, respectively. The binding energy
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38 (per C atom) as a function of the interface distance is given in Fig. 1d. Clearly, the formation
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40 of the MnO₂/graphene interface is exothermic. The three energy profiles almost overlap,
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42 revealing 3.03 Å equilibrium interlayer distance and 90 meV binding energy. This indicates a
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44 weak coupling that is not sensitive to the stacking pattern. In Fig. 1d we show the
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46 spin-resolved band structure of the Mn centered configuration, which is slightly energetically
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48 favorable, at the equilibrium distance. We observe that the electronic properties of the
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components are well preserved, while remarkable new features emerge: The conduction band of MnO_2 crosses the Fermi energy (E_F), giving rise to half-metallicity, and spin polarization arises in graphene by proximity coupling to MnO_2 . The Heyd-Scuseria-Ernzerhof exchange correlation functional⁵⁸ yields the same half-metallic feature for MnO_2 , with the spin majority conduction band crossing E_F . In the following, we aim at exploring the influence of external factors on the material properties and thus investigate graphene/ MnO_2 /graphene and MnO_2 /graphene/ MnO_2 hybrid systems.

We first focus on the graphene/ MnO_2 /graphene system. Contact to graphene results in occupation of states at the conduction band minimum (CBM) of MnO_2 , transforming it into a half-metal. To unravel this transition, we visualize in Fig. 2a the charge redistribution at the interfaces by subtracting the charge of the hybrid system from that obtained for the isolated components. Charge shifts mainly from the interfacial side of the graphene layers towards the two O layers. We note that a weak interfacial interaction does not preclude charge transfer, similar to MoS_2 /graphene.⁵⁹ The CBM is fully spin-polarized and shows contributions of the O $2p$ orbitals.^{44,45} The transferred charge results in half-metallicity, so that a fully spin-polarized electrical current can be realized in MnO_2 in contact to graphene. This constitutes an alternative route to half-metallicity in monolayer MnO_2 besides defect engineering,⁴⁵ which is limited by clustering and/or segregation.⁶⁰⁻⁶²

Since the interfacial interaction is weak, as demonstrated by the large equilibrium distance of 3.03 Å, external perturbations can have a huge effect. Thus, the half-metallic feature is addressed in Figs. 2c-d for varying interlayer distance (D). We find in a wide range around the equilibrium distance still half-metallicity. Compression by $\Delta D = -0.6$ Å remarkably

enhances the orbital overlap so that the Dirac cone is lost and the charge transfer to MnO_2 is reduced (due to the interfacial repulsion). Increasing the separation by $\Delta D = 0.8 \text{ \AA}$ weakens the interfacial interaction and thus the charge transfer, rather surprisingly, only slightly. Accordingly, the Dirac cone is well preserved. The energetic difference between the CBM and E_F in fact reaches a maximum at the equilibrium distance and decreases more sharply when the distance is reduced than when it is expanded, see Fig. 3.

While the effect of out-of-plane strain on the electronic properties is limited, we find that the system can be efficiently tuned by in-plane strain (ϵ). Figures 2e-f show spin-polarized band structures of the graphene/ MnO_2 /graphene system under biaxial strain of -5% and 5%, respectively. The energetic difference between the Dirac point of graphene and the CBM of MnO_2 is larger than before, reflecting more charge transfer. Because tensile strain localizes orbitals, as demonstrated by the enhanced spin splitting of the MnO_2 electronic bands, the orbital overlap at the interfaces is reduced. In Fig. 3 we present the variation of the CBM under strain, showing that the half-metallicity of MnO_2 is always maintained. The energetic difference between the CBM and E_F increases approximately linearly from tension to compression. The modifications are strong enough that it seems feasible to engineer the spin polarization of an electrical current in MnO_2 . We note that strain in many 2D materials can be realized by lattice mismatch to a substrate.⁶³⁻⁶⁷

We next address graphene sandwiched between MnO_2 to explore magnetic proximity effects, adopting the lattice constant of graphene to exclude strain effects. Figure 4b shows the spin-polarized band structure of the MnO_2 /graphene/ MnO_2 system, highlighting the graphene contributions. The case of $\Delta D = -0.6 \text{ \AA}$ is selected as it hosts the most remarkable

effects. The charge transfer, see Fig. 4a, is smaller than in the graphene/MnO₂/graphene system and, interestingly, the charge depletion affects the two sublattices of graphene not to the same degree, so that variation in the onsite energy destroys the degeneracy of the π and π^* bands at the K point. As a result, a band gap of 3 meV is opened at the Dirac point, suggesting a facile way to design nanodevices with both finite band gap and high carrier mobility.⁵⁹

The magnetic proximity effect on graphene due to the presence of MnO₂ is impressive. We find significant spin polarization because of interaction between the π and O 2*p* orbitals (antiferromagnetically aligned to Mn).⁴⁴ The Dirac cone shows a spin splitting of $\Delta E_{\text{Dirac}} = 176$ meV, as demonstrated by the zoomed view of the π bands around the K point in Fig. 5a. Additionally, due to the interlayer coupling, there is still a weak indirect Rashba spin-orbit coupling. As a result, a nontrivial band gap of 1.3 meV is opened between bands of opposite spin when the spin-orbit coupling is switched on. This suggests that the MnO₂ monolayer provides both time-reversal and inversion symmetry breaking. In fact, a quantum anomalous Hall state in graphene can be realized by shifting the Dirac point into the band gap of MnO₂ by alkali metal intercalation, as demonstrated by the band structure shown in Fig. 6.

The proximity effect depends on the magnetic exchange in MnO₂ as well as the orbital hybridization at the interface. The former can be tuned experimentally by applying biaxial strain⁴⁴ and the latter by pressure perpendicular to the interface. Tensile strain enhances the magnetic moments of Mn and O but weakens the orbital overlap and effective interaction between MnO₂ and graphene. The latter effect prevails, thus reducing the proximity effect, as demonstrated by a decreased spin polarization, see Fig. 5b. Compression reduces the

magnetic exchange in MnO_2 but enhances the orbital overlap. The two effects compete with each other, so that the spin polarization reaches a maximum and minimum at $\varepsilon = -1\%$ and -3% , respectively. The spin polarization under strain fluctuates in a narrow range (less than 100 meV). According to Fig. 5b, ΔE_{Dirac} increases sharply when the distance is reduced and decreases moderately when it is enlarged. We obtain an increase by a factor of about 3 for a reduction of 20%. We note that the nontrivial band gap of 1.3 meV resulting from spin-orbit coupling corresponds to a temperature of 15 K. Overall our results show some similarity to the graphene/ BiFeO_3 system,⁴² but in contrast to this case open an avenue to exploring the quantum anomalous Hall effect in all-2D hybrid systems.

4. CONCLUSIONS

We have investigated the MnO_2 /graphene interface and the graphene/ MnO_2 /graphene and MnO_2 /graphene/ MnO_2 hybrid systems. We find that interfacial charge transfer from graphene induces half-metallicity in MnO_2 , which can be strengthened by the application of pressure. In the MnO_2 /graphene/ MnO_2 system time-reversal and inversion symmetry breaking induces a remarkable spin splitting at the Dirac point and a topologically nontrivial gap between bands of opposite spin. The spin splitting and band gap can be enhanced to 176 meV and 1.3 meV, respectively, when the interface distance is reduced by 20%. Our findings can be important in the field of spintronics materials and suggest a venue for observing the quantum anomalous Hall effect in graphene.

Notes

The authors declare no competing financial interest.

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Fig. 1. Top views of the (a) O^{2nd} centered, (b) O^{1st} centered, and (c) Mn centered configurations of the MnO₂/graphene hybrid system. The gray, blue, large red, and small red balls represent C, Mn, O^{1st}, and O^{2nd} atoms, respectively. (d) Binding energy per C atom as a function of the interface distance. Equilibrium distances are indicated by stars. (e) Spin-polarized band structure of the Mn centered configuration at the equilibrium position (red: spin majority, blue: spin minority).

Fig. 2 (a) Charge density difference for the graphene/MnO₂/graphene system. The yellow and cyan regions represent charge depletion and accumulation, respectively. Spin-polarized band structures of the graphene/MnO₂/graphene system at (b) $\Delta D = 0$ Å, (c) $\Delta D = -0.6$ Å, (d) $\Delta D = 0.8$ Å, (e) $\epsilon = -5\%$, and (f) $\epsilon = 5\%$. The circles indicate the bands of MnO₂ (red: spin majority, blue: spin minority).

Fig. 3 CBM as a function of the interlayer distance (blue) and strain (black).

Fig. 4 (a) Charge density difference for the $\text{MnO}_2/\text{graphene}/\text{MnO}_2$ system. The yellow and cyan regions represent charge depletion and accumulation, respectively. (b) Spin-polarized band structure of the $\text{MnO}_2/\text{graphene}/\text{MnO}_2$ system at $\Delta D = -0.6 \text{ \AA}$. The circles indicate the bands of graphene (red: spin majority, blue: spin minority).

Fig. 5 (a) Zoomed view of the black box in Fig. 4 (a), showing only the graphene bands (red: spin majority, blue: spin minority). (b) ΔE_{Dirac} as a function of the interlayer distance (blue) and strain (black).

Fig. 6 (a) Side view of the crystal structure and (b) spin-polarized band structure of the Li intercalated $\text{MnO}_2/\text{graphene}/\text{MnO}_2$ system. The circles indicate the bands of graphene (red: spin majority, blue: spin minority).

TOC Graphic