Robust Magnetoelectric Effect in the Decorated Graphene/\text{In}_2\text{Se}_3 Heterostructure

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ABSTRACT: The magnetoelectric effect is a fundamental physical phenomenon that synergizes electric and magnetic degrees of freedom to generate distinct material responses like electrically tuned magnetism, which serves as a key foundation of the emerging field of spintronics. Here, we show by first-principles studies that ferroelectric (FE) polarization of an In$_2$Se$_3$ monolayer can modulate the magnetism of an adjacent transition-metal (TM)-decorated graphene layer via a ferroelectrically induced electronic transition. The TM nonbonding \(d\)-orbital shifts downward and hybridizes with carbon-p states near the Fermi level, suppressing the magnetic moment, under one FE polarization, but on reversed FE polarization this TM \(d\)-orbital moves upward, restoring the original magnetic moment. This finding of robust magnetoelectric effect in the TM-decorated graphene/In$_2$Se$_3$ heterostructure offers powerful insights and a promising avenue for experimental exploration of ferroelectrically controlled magnetism in two-dimensional (2D) materials.

KEYWORDS: heterostructure, magnetoelectric effect, ferroelectric-controlled magnetism, \(d\)-orbital shifts, first-principles calculations

1. INTRODUCTION

Low-dimensional magnetic materials provide excellent platforms for spintronics that use electron spin rather than charge as the information carrier, and recent years have seen tremendous developments in this emerging field that promises equipment with higher storage density and lower energy consumption.$^{1−3}$ Prototypical spintronic devices have been proposed and demonstrated,$^{4−6}$ but further advances in the field have been hindered by a lack of suitable low-dimensional magnetic materials and adequate means for effective tuning of their magnetic behavior. Recent studies have reported the synthesis of atomically thin two-dimensional (2D) magnets, such as CrI$_3$,$^7$ CrGeTe$_3$,$^8$ Fe$_2$GeTe$_2$,$^9$ and Fe$_2$O$_3$,$^{10}$ but these materials have low Curie temperatures ($\sim$45 K) that limit the scope of their viability. Meanwhile, graphene as the first discovered truly 2D material$^{11}$ has been explored for its magnetic properties,$^{12}$ and magnetism was observed in transition-metal (TM) decorated graphene$^{13−19}$ induced by the hybridization of carbon \(p\) and TM-\(d\) orbitals.$^{20,21}$ Especially notable is the synthesis of suspended TM-decorated single-vacancy graphene (TM@SVG) monolayer$^{22,23}$ with considerably improved stability of well-dispersed TM atoms.

Effective control of magnetism in low-dimensional materials by reliable and convenient means is an essential requirement in spintronics. Among various strategies, electric-field-controlled magnetism is regarded as the most promising.$^{24−28}$ There are three main material-class-specific working mechanisms:$^{28}$ (i) magnetic exchange modulation by electrically tuneable carrier concentration in magnetic semiconductors, (ii) changing coercivity or magnetic anisotropy by shifting the Fermi level in magnetic metals, and (iii) magnetic response to electric tuning via magnetoelectric coupling in multiferroics. Major challenges remain, however, in identifying suitable low-dimensional, mainly 2D, materials with robust magnetism that is responsive to electric-field tuning. An important development in this front is the recently reported synthesis of the In$_2$Se$_3$ monolayer that has proven to be a versatile platform for designing and implementing 2D ferroelectric (FE)-based nonvolatile memory devices$^{29,30}$ and also for facilitating diverse chemical and physical processes, such as photocatalytic water splitting$^{31}$ and magnetic anisotropy modulations.$^{32}$ Its polarization has originated from the asymmetric arrangement of the quintuple layers (see Figure 1a,b), and the orientation can be reversed by the shift of the middle S layer.

In this manuscript, we present computational evidence for a robust magnetoelectric effect in viable TM@SVG/In$_2$Se$_3$ heterostructures, allowing for effective electric tuning of magnetism. The first-principles calculations show that

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magnetic moments derived from TM atoms adsorbed on SVG (V, Cr, Mn@SVG) are highly sensitive to, and therefore effectively controllable by, the switch of FE polarization of the In$_2$Se$_3$ monolayer. This intriguing phenomenon stems from an FE-induced electronic transition that shifts the originally unoccupied nonbonding TM-$d$ states toward the Fermi level to hybridize with the carbon-derived states, thereby largely suppressing the magnetic moment, while a reversal of FE polarization restores the original magnetic state. This electric modulation of magnetism relies on the strong characters of FE polarization of the In$_2$Se$_3$ monolayer, which exerts FE-sensitive electrostatic potentials and associated electron transfers across the interface in the heterostructure. These findings unveil a distinct mechanism for compelling FE-controlled magnetism, making TM@SVG/In$_2$Se$_3$ a promising platform for exploring new magnetoelectric effects in advanced spintronics materials research.

2. METHODS

Spin-polarized electronic structures and total energy calculations have been performed using the Vienna ab initio simulation package (VASP).$_{33,34}$ Computational details are provided in the Supporting Information. The TM@SVG/In$_2$Se$_3$ heterostructure is constructed by matching a $5 \times 5 \times 1$ supercell of SVG with a $3 \times 3 \times 1$ supercell of the In$_2$Se$_3$ monolayer, as shown in Figure 1a,b. The lattice mismatch in this structural model is $0.14\%$, which has only minimal effects on the computed total energies, and structural and electronic properties; this result is also demonstrated by applying the lattice-mismatch strain on In$_2$Se$_3$, but keeping graphene strain-free; see Figure S1. To describe the on-site Coulomb interaction, the Hubbard parameter $U_{e-g}$ is taken as $4$ eV for all of the transition metals based on previously reported results$_{35-37}$ and our tests shown in Figure S2. The In$_2$Se$_3$ monolayer has two distinct faces in contact with graphene, with the FE polarization either pointing upward (P↑) or downward (P↓), as defined in Figure 1b.

3. RESULTS AND DISCUSSION

3.1. Ferroelectric-Tuned Formation Energy and Magnetic Moment. We first examined TM-decorated graphene on In$_2$Se$_3$ (TM@graphene/In$_2$Se$_3$), where the TM atom is adsorbed at the energetically most preferred hexagonal hollow site (see Figure S2a,b), and the FE polarization switch of In$_2$Se$_3$ monolayer produces obvious effects on the total magnetic moments of the system (Figure S2d). For Cr or Mn, the magnetic moments are $0 \mu B$ at TM@graphene/P↑-In$_2$Se$_3$, but become $\sim 4.5 \mu B$ at TM@graphene/P↓-In$_2$Se$_3$ (these magnetic moments are reduced slightly by on-site Coulomb interaction, see Figure S2c). These results demonstrate significant tunability of FE-controlled magnetism. However, TM atoms adsorbed on graphene have low migration energy barriers ($0.2-0.8$ eV$^{21}$) that creates a strong tendency for TM atoms to migrate and form metal clusters, which is detrimental to the stability and functionality of TM@graphene/In$_2$Se$_3$. A promising solution to this issue is offered by the recently synthesized suspended TM@SVG layered structure where the TM atom bonds strongly to the otherwise under-coordinated carbon atoms near the vacancy site in the graphene layer, thus greatly enhancing the stability of the dispersed TM atom configuration and making TM@SVG a viable layered magnetic structure, which can be used to form functional heterostructures with the In$_2$Se$_3$ monolayer. The large diffusion barrier up to 6.8 and 4.5 eV for P↑ and P↓ configurations, respectively (taking Mn@SVG/In$_2$Se$_3$ as an example, see Figure S3), can effectively prevent the formation of TM clusters on the surface. Our calculations show that TM atoms in TM@SVG take out-of-layer equilibrium positions due to their larger radii compared to carbon, which is consistent with previous reports.$^{20,21}$ Meanwhile, the interlayer distance between graphene and In$_2$Se$_3$ is sensitive to the FE polarization of the latter (Figure 1c), which reflects the distinct nature of...
Meanwhile, the small TM atoms (from Mn1 to Mn10) as shown in Figure S5. very large atoms on top of graphene. discussion, we mainly focus on the con
TM@SVG/P
negative as shown in Figure 2 a, indicating that these calculated results for all of the studied TM cases are
S4a,b) since both con
di
calculated formation energies. However, a TM atom is hard to
graphene (Figure 1a,b) or between the graphene and In2Se3 discussed below. TM atoms can locate either on top of
TM@SVG, and the In2Se3 monolayer. This quantity measures
the interaction between the TM@SVG and In2Se3 layers, and the results (see Figure S8) show that the magnetic
moments with the In2Se3 layer in P↑ or P↓ FE polarizations are displayed in Figure 2b, compared with the results for freestanding TM@SVG. It has been proposed20 that these TM@SVG systems mainly fall into three categories: bonding (Sc, Ti), nonbonding (V, Cr, Mn), and antibonding (Co, Ni, Cu, Zn), while Fe represents a special case, sitting between nonbonding and antibonding regimes and exhibiting complex magnetic behaviors. Our calculated results shown in Figure 2b indicate the following: (i) In2Se3 in P↓ polarization has little in
fluence on the magnetic moments of the TM@SVG studied here, with the only exception for Fe@SVG, all of which nearly coincides with the result of the freestanding TM@SVG layer; (ii) for the bonding cases, the TM-d orbitals are fully occupied, rendering zero magnetic moment, independent of the FE polarization of In2Se3, and for the antibonding cases, the results for TM@SVG/P↓-In2Se3, TM@SVG/P↑-In2Se3 and freestanding TM@SVG all stay very close; (iii) the nonbonding cases of V, Cr, and Mn@SVG/In2Se3 possess magnetic moments that are sensitively dependent on the FE polarization of In2Se3. For example, the magnetic moment is 2.9 μB at Mn@SVG/P↓-In2Se3 but only 0.12 μB at Mn@SVG/P↑-In2Se3. It is worth noting that the total magnetic moments in TM@SVG/In2Se3 systems are mainly contributed by TM atoms, while a small portion of magnetic moments comes from the three nearest carbon atoms with opposite spin polarization (the values on TM and carbon atoms are shown in Figure S7). To probe the origin of these sharply contrasting behaviors, we have artificially tuned the distance between Mn@SVG and In2Se3 layers to test the influence of the interlayer interaction, and the results (see Figure S8) show that the magnetic moment of Mn@SVG/P↓-In2Se3 increases with the increasing interlayer distance, suggesting a strong interlayer effect on the magnetism of the Mn@SVG layer, and the value approaches that of the freestanding TM@SVG at large interlayer distances when the effect of the In2Se3 layer on the TM@SVG diminishes. Meanwhile, the magnetic moment of Mn@SVG/ P↓-In2Se3 remains largely unchanged throughout this process, indicating little influence by the interlayer interaction. The FE polarization-dependent magnetism is also seen in spatial spin distributions, where a larger number of unpaired electrons gather around the Mn site in the case of Mn@SVG/P↓-In2Se3, while a much smaller spin density appears in the case of Mn@SVG/P↑-In2Se3 (see insets of Figure 2b).

Figure 3. (a) Electron transfer based on a Bader charge analysis between TM@SVG and In2Se3 layers in TM@SVG/In2Se3 heterostructures. (b) The differential charge density of Mn@SVG/In2Se3 heterostructures with P↑ and P↓ FE polarization in the In2Se3 layer. The isosurface value is set to 0.0002 eV/Å³. (c) The electrostatic potential profile for Mn@SVG/In2Se3 and the potential differences between graphene and contacting In atoms for the two polarizations. Vertical green lines are plotted to indicate the electrostatic potential difference for opposite sides of the heterostructure.
3.2. Ferroelectric-Dependent Electron Transfer. To check the dependence of the calculated interlayer interaction and the associated magnetic behaviors on the choice of the vdW potential, we have performed additional calculations using the Tkatchenko–Scheffler (TS) and DFT-D3 method with Becke–Johnson damping methods. For the exemplary case of Mn@SVG/In2Se3, we find that although the magnitude of magnetic moments does vary quantitatively with the choice of potentials, the overall behaviors remain unchanged (for details see the results presented in Table S1).

The sharply contrasting behaviors of the formation energy and magnetic responses of the TM@SVG/In2Se3 heterostructures presented above can be understood in terms of the interfacial charge transfer and the resulting shift of the TM d orbital under distinct FE polarization of the In2Se3 monolayer. The results of a Bader charge analysis (Figure 3a) indicate that opposite FE polarizations have a significantly distinct influence on the electron transfer between the TM@SVG and In2Se3 layers. When In2Se3 is in the P↑ polarization, only 0.03e is transferred to TM@SVG from In2Se3, which acts as an electron donor. In sharp contrast, In2Se3 becomes an electron acceptor to receive a much larger amount (~0.2e) of charge transfer from the TM@SVG layer when the polarization is reversed to P↓. This drastically increased electron transfer leads to much stronger interfacial interaction, as reflected in the greatly enhanced formation energy (Figure 2a). For an intuitive understanding, we take Mn@SVG/In2Se3 as an example to analyze the spatial charge density difference ∆ρ = ρtotal − ρIn2Se3 − ρSVG = ρMn. The results (Figure 3b) show that in P↑-In2Se3 electron transfer occurs mostly from the Mn atom to SVG with only a minimal amount from the In2Se3 monolayer, whereas in P↓-In2Se3 there is a considerable amount of electron transfer from the Mn atom to the In2Se3 monolayer through the contacting SVG layer. This result can be ascribed to the larger electrostatic potential difference (18.74 vs 17.03 eV) at the interfaces of the heterostructure as shown in Figure 3c, and also electrostatic potential differences on the opposite sides of the heterostructures (2.01 vs 0.88 eV) due to the FE polarizations in In2Se3 layers, where the surface of the In2Se3 monolayer with lower electrostatic potential is in close contact with the Mn@SVG layer.

3.3. Mechanism of Magnetism Tuned by Ferroelectricity. The FE-controlled magnetic behaviors (Figure 2b) can be further elucidated by examining pertinent chemical bonding changes and the spin-polarized density of states (DOS) of the adsorbed TM atom under different polarizations of the In2Se3 monolayer. Since most of the magnetic moment is contributed by the TM and the surrounding carbon atoms, it is instructive to analyze the TM-C bond length and the associated band shifts. We show in Figure 4a the calculated TM-C bond lengths, and the results indicate that the TM-C bond length first follows a descending trend in going from 2.10 Å (Sc) to 1.75 Å (Co), and then moves upward and increases to 1.90 Å (Zn); the same trend is seen in freestanding TM@SVG. For most cases, the bond lengths between the adsorbed TM atom and the three nearest-neighbor carbon atoms remain nearly unchanged under the switch of FE polarization, so the C(sp2) symmetry at the TM-adsorbed carbon vacancy site in SVG is preserved during the FE switch. Notable differences, however, exist in the TM-C bond length for the cases involving the nonbonding states (V, Cr, Mn). This pattern in bond-length variations corroborates with the behaviors of the magnetic modulation by FE polarization (Figure 2b). These shorter TM-C bonds enhance the hybridization between the TM-d and carbon-p states, thereby asserting a stronger influence on the magnetic moment of the TM@SVG-In2Se3 heterostructure.

For a more in-depth assessment of the driving mechanism for the magnetic responses, we have examined the partial density of state (PDOS) of the Mn-d orbital and its hybridization with the p orbitals of the surrounding nearest-neighbor carbon atoms. The calculated spin-polarized PDOS for Mn@SVG/In2Se3 in both polarizations are shown in Figure 4c, together with the results for freestanding Mn@SVG for comparison. It is seen that in Mn@SVG/P↑-In2Se3 the shortening of the Mn-C bonds leads to a large downward shift of the Mn-d orbital, which is located 0.655 eV above the Fermi level in freestanding Mn@SVG, to the vicinity of the Fermi level. As a result, the originally unoccupied nonbonding Mn-d state is now partially occupied and hybridizes with the nearest C-p states near the Fermi level. This large shifting of the Mn-d state considerably reduces the spin splitting and, therefore, the associated magnetic moment. Similar mechanisms have been invoked in previous studies to explain the relationship between carbon vacancies and the induced magnetism. In sharp contrast, after the FE polarization of the heterostructure is switched to the reversed direction, the Mn-d state in Mn@SVG/P↓-In2Se3 moves upward in energy from its original position to be further away, located at 1.06 eV above the Fermi level, accompanied by a slight shift of the C-p states toward the Fermi level. Under this circumstance, there is no hybridization...
between the Mn-d and C-p orbitals, and the pertinent nonbonding Mn-d state remains unoccupied, thus leaving the magnetic moment of the heterostructure unaffected in P↓ -In2Se3, despite the resulting increase in the spin splitting of the Mn-d states. To confirm the reliability of the analysis about orbital hybridization, we calculated the DOS and magnetic properties of freestanding 3X3X1 Mn@SVG (shown in Figure S9a) using the Heyd−Scuseria−Ernzerhof (HSE)\(^{41}\) functional to verify if the standard Perdew−Burke−Ernzerhof (PBE) results can capture the main underlying physics. The total spin moment of freestanding Mn@SVG is 2.679 \(\mu_B\) calculated using the HSE functional, which is the same as the PBE result. Besides, the spin-polarized partial DOS plotted in Figure S9b shows no hybridization between the Mn-d and C-p orbitals near the Fermi level, and therefore, the pertinent nonbonding Mn-d state remains unoccupied and results in the magnetic moment for Mn@SVG. These results indicate that PBE simulations can well capture the main physics, and the findings reported here are reliable. This mechanism also renders similar phenomena of FE polarization modulation in Cr@SVG/In2Se3 (see Figure S10). In the P↑ FE polarization of the In2Se3 monolayer, the Cr-d state shifts downward toward the Fermi level and hybridizes with the C-p states, resulting in the diminished total magnetic moment in the heterostructure. In contrast, when the FE polarization is reserved to P↓, the nonbonding Cr-d state moves upward and remains unoccupied, thus not affecting the magnetism. These results suggest that the reversible FE polarization of the In2Se3 monolayer can act as an effective control for the magnetism of TM@SVG in a heterostructure configuration, which is highly promising for feasible and convenient modulation of 2D magnetism that may facilitate the innovative design and implementation in novel spintronic operations.

The phenomena revealed here, namely the ferroelectric-controlled magnetism and magnetoelectronic coupling in the 2D heterostructures, are interesting and promising for the next-generation spintronic devices. However, for practical applications, several issues still need to be discussed and solved, such as the detection of magnetic orders in low-dimensional materials and the polarization reversal in ferroelectrics. Recent experimental developments have laid solid foundations for the associate dominant contributions to the magnetic moment.

Since freestanding magnetic TM@SVG and ferroelectric In2Se3 monolayer structures both have been experimentally synthesized and characterized, it is reasonable to expect that the construction of the heterostructure based on these 2D materials is practically feasible. The intricate working mechanisms unveiled in the present work may help develop other layered material structures in the fast-growing family of 2D materials possessing diverse electric and magnetic behaviors that could combine to form heterostructures with pronounced magnetoelectric effect, thus further advancing and expanding the material basis for the fast-growing field of spintronics research and development.
SVG-P↓-In$_2$Se$_3$ heterostructure; formation energy $E_{TM,form}$ with charge distributions of Mn@SVG/P-In$_2$Se$_3$ total magnetic moments and spin moments distributed on Mn and the nearest three carbon atoms variation of magnetism as a function of artificially increased interlayer distance dependence of FE-controlled magnetic moments on the choice of van der Waals corrections; calculated spin-polarized DOS for $3 \times 3 \times 1$ Mn@SVG calculated using the HSE 06 hybrid functional PDOS shifts in the Cr@SVG/In$_2$Se$_3$ heterostructure; influence of O$_2$ and H$_2$O molecules on magnetic properties for Mn@SVG/P-In$_2$Se$_3$ and also contains refs 1–6 (PDF)

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#### Notes

The authors declare no competing financial interest.

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