Two-dimensional hexagonal manganese carbide monolayer with intrinsic ferromagnetism and half-metallicity

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Keywords: first-principles, two-dimensional materials, intrinsic ferromagnetism, room-temperature half-metallicity, van der Waals heterostructures, spintronics

Abstract

Recent experimentally observed intrinsic ferromagnetism in two-dimensional (2D) van der Waals crystals has ignited substantial interests due to their great potential in spintronic devices. However, their practical applications are hampered by rather low Curie temperature and small magnetic anisotropic energy. Here, we predict from first-principles calculations that the 2D pristine hexagonal manganese carbide (h-MnC) sheet exhibits robust ferromagnetic and half-metallic features with complete spin polarization, sizable magnetic anisotropic energy, and wide half-metallic gap near the Fermi energy level. Moreover, the h-MnC sheet can retain its structure up to the temperature of 1000 K, indicating a highly thermodynamic stability. The Monte Carlo simulations based on the Heisenberg model with single-ion anisotropy predict a Curie temperature of 233 K in 2D h-MnC crystal. We confirm the robustness of the ferromagnetism and half-metallicity against the external strain from −6% to 10%. Also, a feasible experimental fabrication route is proposed to realize the h-MnC monolayer via heterostructure engineering and exfoliation techniques. Overall, the robustness of the half-metallicity in combination with the high-temperature ferromagnetism render the freestanding h-MnC monolayer and even its energetically favorable h-MnC/MoS2 and h-MnC/MoSe2 heterostructures quite promising materials for developing practical spintronic nanodevices.

1. Introduction

Since the discovery of graphene, two-dimensional (2D) materials have aroused considerable interests in the scientific community not only because of their novel physics arising from quantum confinement effects but also of their great prospect in various applications [1–4]. However, a majority of 2D materials like graphene [5], hexagonal boron nitride (h-BN) [6], phosphorene [7], transition-metal dichalcogenides (TMDCs) [8], are intrinsically nonmagnetic or weakly magnetic in their pristine forms, which has consequently blocked their potential application in spintronics. To realize such an application at nanoscale, one key issue is to require 2D materials having the ability of formation of robust ferromagnetism and large spin polarization. Half-metallic ferromagnets, which have a metallic nature in one spin channel and an insulating or semiconducting character in the other, are considered to be the most promising spintronic materials to intrinsically provide complete spin polarization [9]. As a consequence, the pursuit of ferromagnetic ordering as well as half-metallic feature of 2D materials remains an urgently desired goal for the fabrication of practical spintronic devices.

During the past decades, a number of various approaches have been proposed to extrinsically create possible ferromagnetism and half-metallicity in pristine nonmagnetic materials by means of surface functionalization [3, 10–12], defect engineering (e.g., adatoms, dopants, vacancies, zigzag or armchair edges) [2, 13–16], spin injection [2, 17, 18], strain engineering [19, 20], and electric field [21, 22]. Although
these external manipulations can be more or less achieved experimentally, their precise control is beyond the capability of current technology and still facing many challenges [9, 23]. At the same time, the resulting systems may well suffer from serious shortcomings, such as low Curie temperature and weak spin interaction, so that producing ordered ferromagnetic and half-metallic properties may be easily destroyed by thermal fluctuations, far from practical room temperature spintronic application. To prevent the half-metallicity from the thermally agitated spin-flip transitions, the magnetic ordering of practical spintronic materials must be sufficiently robust to survive above room temperature. Inspired by the recent experimental observations of intrinsic ferromagnetism in 2D CrI3 and Cr2Ge2Te6 crystals [24, 25], there are considerable efforts on the theoretical side on identifying intrinsic pristine rather than extrinsic tailored 2D ferromagnetic materials to realize such an exotic half-metallic state that will meet the above spintronic requirements [26–34]. It is much interesting to note that depending on its polymorphic form, 2D VN crystal can exhibit different electronic structures. In more detail, the t-VN sheet possesses metallic character, whereas h-VN demonstrates its half-metallic nature of conductivity [27]. To the best of our knowledge, while t-MnC has been similarly predicted to be a stable monolayer metallic ferromagnet [12], the electronic and magnetic properties of 2D h-MnC crystal have not yet been investigated.

In this work, we have carried out comprehensive density functional theory (DFT) calculations to systematically investigate the novel h-MnC monolayer for making clear its potential application in spintronic nanodevices. We first confirm its thermodynamic stability up to 1000 K, evincing the possibility to experimentally produce the h-MnC monolayer. More strikingly, we then show that the pristine h-MnC monolayer is a half-metallic ferromagnet at its ground state with complete spin polarization at Fermi energy level, considerable magnetic anisotropic energy and large net magnetic moment of 3 μB per unit cell. Also, the h-MnC sheet exhibits the Curie temperatures up to around 200 K and wide electronic energy band gaps in the absence and presence of moderate biaxial strains. Finally, we propose a viable experimental realization route to fabricate the freestanding h-MnC monolayer via heterostructure engineering and exfoliation techniques commonly employed in other 2D van der Waal crystals.

2. Computational methodology

All atomic and electronic structure calculations are carried out by means of the Vienna \textit{ab initio} simulation package [35, 36] in the framework of the generalized gradient approximation using the Perdew–Burke–Ernzerhof exchange-correlation functional [37]. The projector augmented wave pseudopotential is adopted with a cutoff energy of 500 eV for plane-wave expansions [38]. The electron configurations of Mn and C atoms take 3p^4 4s^2 3d^5 and 2s^2 2p^2, respectively. To properly account for the strong-correlation effects in the transition-metal Mn atoms, Hubbard U correction is adopted within the rotationally invariant DFT + U approach [39]. Unless otherwise stated, we select a typical value of U = 4 eV from recent literature [26, 29]. The impact of U values on the magnetic moment per unit cell is studied by changing U values from 1.0 eV to 9 eV for h-MnC monolayer, which shows that the magnetic moment remains the same for all U values with an almost linear change in the lattice constant (figure S1† in supporting information (https://stacks.iop.org/NJP/22/103049/mmedi a)).

The screened hybrid Heyd–Scuseria–Ernzerhof (HSE06) functional is employed to obtain more accurate band structures [40]. A vacuum separation of 15 Å thickness is applied to eliminate any artificial interactions between the neighboring periodic images. A Γ-centered Monkhorst–Pack scheme with k-point mesh of 11 × 11 × 1 in the Brillouin zone is used for structure optimization and for the calculations of electronic and magnetic properties, respectively. The convergence criteria for energy and force are set to 10^{−6} eV per atom and 0.01 eV Å^{−1}, respectively. The phonon dispersion spectrum is calculated by density functional perturbation theory [41] as embedded in the PHONOPY package [42]. \textit{Ab initio} molecular dynamics (AIMD) simulations are carried out in canonical ensemble up to 5 ps with a time step of 1.0 fs using a 5 × 5 × 1 supercell of the h-MnC monolayer, during which the temperature of the system is maintained at 300 or 1000 K by using a Nosé–Hoover thermostat [43]. Grimme D3 correction of total energy is considered to incorporate the long-range van der Waals interactions for multilayer heterostructure systems [44].

3. Results and discussion

Our systematic investigation begins from the geometry and stability of the h-MnC monolayer. The proposed graphene-like atomic structure with P6m2 symmetric group is depicted in figure 1(a) for the case of U = 4 eV, in which the h-MnC unit cell is bordered using black lines with the optimized lattice constant being a = 3.35 Å and the equilibrium Mn–C bond length being 1.94 Å, respectively. To ascertain the
Figure 1. (a) Top and side views of optimized geometric structure. Black rhombus denotes the unit cell and the arrows show the lattice vectors. (b) Phonon spectrum. The slope of black dashed lines near the $\Gamma$ point represents the sound speed for the LA phonons. (c) and (d) Top and side views of characteristic snapshots taken from the AIMD simulations at 300 and 1000 K up to 5 ps within the canonical ensemble.

The structural stability of the $h$-MnC monolayer, the cohesive energy is calculated using the formulas

$$E_{\text{coh}} = \left( E_{\text{Mn}} + E_{\text{C}} - E_{\text{MnC}} \right) / 2$$

where $E_{\text{Mn}}$ and $E_{\text{C}}$ are the energies of isolated Mn and C atoms, $E_{\text{MnC}}$ is the total energy of 2D $h$-MnC unit cell. The calculated cohesive energy is 3.67 eV per atom. This value is lower than those of MoS$_2$ (5.05 eV per atom) [45] and graphene (7.85 eV per atom) [5], as well as close to those of silicene (3.94 eV per atom) [46] and black phosphorene (3.48 eV per atom) [47]. These comparisons with experimentally synthesized monolayers indicate the possible stability of 2D $h$-MnC monolayer.

The dynamical stability of the $h$-MnC monolayer is evaluated with its phonon spectrum. As shown in figure 1(b), the absence of imaginary frequencies in the entire Brillouin zone confirms that the material is dynamically stable and may exist as a freestanding 2D crystal. As expected, the out-of-plane acoustic (ZA) branch shows a quadratic dependence upon the wave vector, which is a typical feature of 2D materials [48], while the longitudinal acoustic (LA) branch exhibits a linear dependence. The speed of sound for the LA phonons gives nearly the same value ($\approx 6.8$ km s$^{-1}$) along the $\Gamma$-M and $\Gamma$-K directions, indicating that the $h$-MnC monolayer is almost elastically isotropic. On the other hand, this value is smaller than those of blue phosphorene ($\approx 8.1$ km s$^{-1}$) [49] and graphene ($\approx 21.2$ km s$^{-1}$) [50], revealing that this material has relatively weak in-plane stiffness and therefore facilitates the strain engineering of its physical properties.

The elastic constants are calculated to further confirm the mechanical stability. Our obtained elastic constants are $C_{11} = C_{22} = 53$ N m$^{-1}$, $C_{12} = 50$ N m$^{-1}$, and $C_{44} = 1.50$ N m$^{-1}$, respectively. The common Born criterion for judging mechanical stability of 2D hexagonal crystals requires $C_{11} > 0$, $C_{22} > 0$, $C_{44} > 0$, and $C_{11}C_{22} - C_{12}^2 > 0$ [28]. Our results clearly satisfy this criterion, guaranteeing that the $h$-MnC monolayer would be grown experimentally even when it is subject to the lattice mismatch with possible substrates.

To corroborate the thermal stability of $h$-MnC at elevated temperatures, we have performed AIMD simulations in the canonical ensemble with a Nosé–Hoover thermostat at 300 and 1000 K, respectively. The snapshots in figures 1(c) and (d) illustrate that the final atomic configurations of these two targeted temperatures after annealing for 5 ps keep the original hexagonal honeycomb structure well. We do not observe any structural decomposition except for some very slight puckers. Small fluctuations in the free energy with respect to the time during entire AIMD simulations further verify the thermal stability of the $h$-MnC monolayer (figure S2†). These results are consistent with the high cohesive energy of the new proposed $h$-MnC monolayer and show that the structure is expected to be thermally stable at high
temperature at least up to 1000 K, which is crucial for experimental fabrication and various room temperature spintronic applications.

We are next planning to perform the chemical bonding analysis of 2D $h$-MnC monolayer. The Bader charge analysis [51] reveals that there is an average of 1.14 e charge transfer from a Mn atom to its neighboring C atoms. As seen from figure 2(a), charge is mainly distributed over C atoms. The shape of charge spatial distribution refers to in-plane orbitals responsible for the formation of the Mn–C bonds. The deformation charge density distribution in figure 2(b) clarifies a significant charge transfer from Mn to C atoms. Charge accumulation takes place around C atoms while charge depletion surrounds Mn atoms. Obviously, there is almost no charge (marked by green) in between the Mn and C atoms, indicating that strong ionic Mn–C bonds are formed in 2D $h$-MnC crystal. To further understand the bonding characteristics, we calculate the electron localization function (ELF) as a contour picture in real space with values ranging from 0.0 to 1.0. Note that the values with 0.0 and 1.0 indicate the charge-deficient and charge-rich regions, respectively. The calculated ELF isosurfaces are depicted in figure 2(c), from which one can find that the valence electrons are localized around C atoms while they are depleted from Mn atoms, reflecting an ionic bonding nature. The form of electron localization in the plane of the monolayer reveals that the orbitals of C atoms are characterized by $sp^2$ hybridization. On the other hand, the $p_z$ orbitals of C atoms perpendicular to the atomic plane refer to the green part of ELF contour maps, implying the probability of free electron gas [52]. Therefore, the weak overlap still exists of charge density between the Mn and C atoms, which indicates a covalent character to some extent. In sharp contrast to the nonpolar covalent bonding in graphene where electrons are shared more equally among C atoms, the $h$-MnC monolayer has an overall ionic nature due to the difference in electronegativity between the Mn and C atoms [53].

Let us now discuss the electronic properties. Various magnetic states, involving ferromagnetic (FM) and antiferromagnetic (AFM) coupling orders, are considered to determine whether the FM state is energetically more favorable. Our calculations show that the FM configuration is 0.60 eV lower in energy than the AFM state per unit cell. It is therefore found that the ground state of the $h$-MnC monolayer has a substantial FM ordering. Note that the ferromagnetism stemming mainly from the Mn 3$d$ orbitals near the Fermi level is an intrinsic feature, which does not need any extrinsic chemical or structural modifications. The spin-polarized band structure and the total density of states (DOS) of the FM phase are presented in figure 3 (a) at the HSE06 level for better evaluating the electronic performance of the $h$-MnC monolayer. The spin-up bands (red curves) cross the Fermi level and thus display a metallic character, whereas the spin-down channel (blue curves) behaves as a semiconductor with an energy gap around the Fermi level of $E_g = 3.72$ eV. Consequently, we predict that the $h$-MnC monolayer is an intrinsic half-metallic ferromagnet and thus has complete spin polarization near the Fermi level. Also, the half-metallicity is supported by the calculated band structures and total DOS from the DFT+U functional (figure S3†), while this rough scheme yields a gross underestimation in the energy gap ($E_g = 2.55$ eV) by 31.5%.

To keep the half-metallicity at room temperature, the half-metallic gap, which is defined as the minimum between the lowest energy of conduction bands with respect to the Fermi level and the absolute value of the highest energy of valence bands [54], should be sufficiently wide to provide a great capability for the prevention of the thermally excited spin-flip transitions. According to the definition in combination with figure 3(b), one can find that the gap is $E_i = 1.36$ eV at the HSE06 level, which is much greater than the other large half-metallic gaps of CaC (0.83 eV), SrC (0.81 eV), and BaC (0.61 eV) [54]. The intrinsic half-metallicity with wide half-metallic gap renders the $h$-MnC monolayer a natural candidate for future applications in spintronics.
Figure 3. (a) Band structure and DOS at the HSE06 level. Red and blue curves represent the spin-up and spin-down states, respectively. (b) Schematic illustration of half-metals. Up and down arrows denote the spin-up and spin-down polarization, respectively. \( E_g \), \( E_1 \), and \( E_2 \) refer respectively to energy gap, CBM, and VBM.

Table 1. Summary of magnetic anisotropy energies per Mn atom of various directions against the [001] direction.

| Direction   | Energy (\( \mu eV \)) |
|-------------|-----------------------|
| [100] − [001] | 258                   |
| [010] − [001] | 258                   |
| [110] − [001] | 256                   |
| [111] − [001] | 172                   |

Also, the magnetic anisotropy energy (MAE) of 2D materials, which arises mainly from the spin–orbit coupling (SOC) effect, is very important to establish the thermal stability of long-range magnetic order. To determine the easy and hard magnetization axes, SOC calculations are carried out on the \( h \)-MnC monolayer along the in-plane [100], [010], and [110] directions as well as the out-of-plane [001] and [111] directions. The energy difference as summarized in table 1 clearly shows that the easy axis of 2D \( h \)-MnC crystal is along the out-of-plane [001] direction. In more detail, the calculated MAE along the [001] direction is lower in energy than those along the [100], [010], [110], and [111] directions by 258, 258, 256, and 172 \( \mu eV \) per Mn atom, respectively. And these magnitudes are two orders larger than those of commonly used FM materials such as Fe (1.4 \( \mu eV \) per atom) and Ni (2.7 \( \mu eV \) per atom) bulks [55]. The sizable MAE values imply that 2D \( h \)-MnC crystal has promising applications in magnetic storage devices.

Another critical parameter for the practical application of half-metallicity in spintronic devices is the Curie temperature (\( T_C \)) of FM materials. Traditionally, it is possible to predict \( T_C \) from the mean-field approximation (MFA). However, the MFA often gives an overestimation of the actual ordering temperature for its neglect of the effect of spin fluctuations [56]. The more accurate estimation can be made using statistical Monte Carlo (MC) simulations based on the Heisenberg model. The classical spin Hamiltonian is defined as [57, 58]

\[
H = -\frac{1}{2} \sum_{i,j} S_i \cdot S_j - A(S_i^{[001]})^2
\]

where \( J \) is the nearest magnetic exchange coupling constant, \( S_i \) and \( S_j \) are the spin operators on two nearest-neighboring \( i \) and \( j \) sites, \( A \) is the single-ion anisotropy energy parameter, and \( S_i^{[001]} \) is the spin component of site \( i \) along the [001] direction. The \( J \) value can be evaluated from the exchange energy \( E_{\text{ex}} = E_{AFM} - E_{FM} \) between the AFM and FM spin arrangements as shown in figures 4(a) and (b) according to the following equations in the unit cell of 2D \( h \)-MnC crystal

\[
E_{FM} = E_0 - 3J|S|^2 - A|S|^2
\]

\[
E_{AFM} = E_0 + J|S|^2 - A|S|^2
\]

where \( E_0 \) refers to the total energy exempt from the magnetic coupling. Therefore, \( J \) is calculated here to be 16.67 meV. The single-ion anisotropy \( A \) is determined to be 28.7 \( \mu eV \) by

\[
A = \frac{E_{[100]} - E_{[001]}}{|S|^2}.
\]
temperatures under consideration. One can see from figure 4(c) that $T_C$ can be estimated to the value between 200 K at which the magnetic moment of 2D $h$-MnC crystal starts dropping sharply and 250 K at which the paramagnetic state is achieved. More precisely, the $T_C$ of 2D $h$-MnC crystal is found to be 233 K via locating the peak position in the magnetic susceptibility curve, which is remarkably higher than the recently reported in experiment CrI$_3$ monolayer (45 K) [24] and Cr$_2$Ge$_2$Te$_6$ bilayer (30 K) [25]. The high $T_C$ means that the $h$-MnC monolayer may be a promising candidate for spintronic applications. On the basis of the same procedure, our obtained $T_C$ is 46 K for the synthesized CrI$_3$ monolayer (figure S4†), which indicates a remarkable degree of consistency with the experimental value of 45 K [24], confirming the reliability of our procedure.

The preservation of both robust ferromagnetism and intrinsic half-metallicity in the $h$-MnC monolayer under strain is very important for further synthesis and spintronic applications. Moving further, we systematically study the evolution of energetics, structural parameter, electronic and magnetic properties of the $h$-MnC monolayer under various biaxial strains. The obtained results are presented in figure 5 by the DFT + $U$ method. Also, we calculate the total DOS (figure S5†) of these strained $h$-MnC monolayers at the HSE06 level for validating those results obtained by the DFT + $U$ approach. Here, the strain is defined as

\[ \varepsilon = \frac{a - a_0}{a_0} \]  

where $a$ and $a_0$ are the lattice constants in the presence and absence of strain. Note that the negative and positive $\varepsilon$ values refer to the compressive and tensile strains, respectively. Considering the experimental operations and practical applications of nanoscale spintronic devices, we only focus on the variation of biaxial strains from $-10\%$ to $10\%$. Figure 4(a) shows that the energy difference between the AFM and FM phases is always greater than zero, indicating that the ferromagnetism of the $h$-MnC monolayer is robust against external strain. Apart from some slightly decrease at the compressive strain greater than $6\%$, the magnetic moment per unit cell of the $h$-MnC monolayer remains unchanged. We further estimate the dependence of the Curie temperature with respect to strain. As seen from figure 4(b), there is a point slightly away from the equilibrium under zero strain toward tensile strain, at which the Curie temperature exhibits a peak. The indicator shows that the Curie temperature can be further enhanced with the introduction of small tensile strain. Beyond this point of local maximum, the Curie temperature tends to decrease, regardless of the type of biaxial strain. Also, a similar strain dependence is observed of the energy difference between the AFM and FM states. Overall, all $T_C$ values retain around 200 K within the $\pm 10\%$ strain range. Such behavior change in $T_C$ with the external strain can be understood with the structural deformation of 2D $h$-MnC crystal. As expected, one can clearly appreciate from figure 4(b) that the lattice constant changes linearly with strain, which in combination with the observation from figure 4(a) that the magnetic moment per unit cell remains unchanged except for a nearly linear decrement with the enhanced compressive strain from $-6\%$ to $-10\%$, shows that moderate lattice mismatch between the $h$-MnC monolayer and substrate materials in the experimental synthetic process does not affect its magnetism at all.

According to figure 5(c), the conduction band minimum (CBM) of the spin-down channel crosses the Fermi energy level upon compression from $-6\%$ to $-10\%$, implying that biaxial deformation of 2D $h$-MnC crystal destroys its half-metallicity. However, it is of much interest to find that for the strain varying from

![Figure 4. Spin density isosurface plots for (a) FM and (b) AFM spin arrangements. The isosurface level is set to be 0.01e/a$_0^3$ with a$_0$ being the Bohr radius. The red and green isosurfaces correspond to the up- and down-spin states, respectively. (c) The simulated magnetic moment per unit cell and magnetic susceptibility with respect to temperature.](image)
Figure 5. Strain dependence of (a) energy difference between the AFM and FM phases based on a $2 \times 2 \times 1$ supercell and magnetic moment per unit cell, and of (b) lattice constant and Curie temperature, as well as of (c) band edges and (d) energy gap of the spin-down channel.

$-6\%$ to $10\%$, the large energy gap of the spin-down channel and the metallic spin-up channel are fully maintained in these strained $h$-MnC monolayers, also see figures 4(d) and S5†, demonstrating their half-metallic nature and thus complete spin polarization near the Fermi energy level. In addition, it is appreciable from figures 4(c) and (d) that the obtained CBM edges remain almost identical under different strains by the HSE06 and DFT $+ U$ approaches, whereas the edges of valence band maximum (VBM) and the energy gap at the HSE06 level are greater than those obtained by the DFT $+ U$ approach. Despite the discrepancy appearing in the VBM edges and the energy gap, we recognize that the observed general trends display similar behavior, regardless of the choice of the used approaches. As such, both HSE06 and DFT $+ U$ are appropriate for describing the variation in the band gap [28]. On the basis of the above analyses, it is reasonable to conclude that the $h$-MnC monolayer shows a stable FM character and robust half-metallicity under the realistic moderate strains from $-6\%$ to $10\%$. As a consequence, our predicted $h$-MnC monolayer is quite promising to be used for advanced spintronic applications where the stable half-metallic ferromagnetism against strain is highly desirable in the ambient environment.

Finally, it is natural to consider how to prepare 2D $h$-MnC crystal in experiment. Creating the van der Waals heterostructures via the chemical or physical vapor deposition methods on the appropriate substrates has been widely used as a versatile strategy for the stacking fabrication of different 2D materials [17, 59–62]. As discussed before, the in-plane elasticity of the $h$-MnC monolayer and its insensitive response to external strains under moderate intensity make it unnecessary to perfectly match the structural parameters of the $h$-MnC monolayer with candidate substrates in the lateral translation vectors. Moreover, it is well-known that TMDs MX$_2$-based semiconductor devices via heterostructure engineering have been successfully realized for modern electronic and spintronic applications [17, 59–61]. We therefore believe that the 2D $h$-MnC/MX$_2$ heterostructures are promising to remain robust ferromagnetic and half-metallic nature of the $h$-MnC monolayer.

To facilitate the experimental preparation, we take MoS$_2$ and MoSe$_2$ as tailored substrates to hold the $h$-MnC monolayer. The calculated lattice constant is $3.18$ Å for the MoS$_2$ monolayer and $3.32$ Å for the MoSe$_2$ monolayer, in excellent agreement with previous theoretical values [63] and experimental data [64, 65]. The lattice of the $h$-MnC monolayer has a major $5.2\%$ mismatch with the MoS$_2$ monolayer and a minor $0.9\%$ mismatch with the MoSe$_2$ monolayer. Generally speaking, the small mismatch around $1\%$ may be more suitable for vertical stacked heterostructures [27]. It should be stressed in our case that the big $5.2\%$ mismatch between the $h$-MnC and MoS$_2$ monolayers is deliberately adopted to tolerate large external strain. To search for the most energetically favorable heterostructure, there are six types of possible
configurations based on different arrangements of the $h$-MnC monolayer on the top of the MoS$_2$ or MoSe$_2$ substrates (figure S6†). Grimme D3 correction of total energy is used to include the effect of van der Waals interactions [44]. According to table SI†, the lowest energy type-(d) configuration of both $h$-MnC/MoS$_2$ and $h$-MnC/MoSe$_2$ heterostructures corresponds to the one in which the Mn atoms are located directly above either S or Se atoms and the C atoms are situated above the centers of either MoS$_2$ or MoSe$_2$ hexagons.

In figure 6, we show the spatial spin density distributions of the $h$-MnC/MoS$_2$ and $h$-MnC/MoSe$_2$ heterostructures in their most favorable configurations. It indicates that the $h$-MnC FM ordering is perfectly retained in both cases, where the ferromagnetism is mainly localized around the Mn atoms while the C atoms carries small opposite spin moments. The magnetic behavior is not found to transfer from the $h$-MnC monolayer to the MoS$_2$ and MoSe$_2$ substrates. Also, we present the band structure and the total DOS at the HSE06 level. As shown in figure 7, one can clearly see the typical half-metallic character, yielding complete spin-polarized electrons at the Fermi level. A metallic behavior takes place in the spin-up channel while a direct energy gap in the spin-down channel is well above 1.80 eV for both $h$-MnC/MoS$_2$ and $h$-MnC/MoSe$_2$ heterostructures. These large energy gaps in combination with the half-metallic gaps of 0.10 eV for $h$-MnC/MoS$_2$ and 0.16 eV for $h$-MnC/MoSe$_2$ in the semiconductive channel can effectively prevent the spin-flip transitions, and further show that such heterostructures may be compelling candidate materials for spintronics. It is important to point out that the FM ordering and in particular half-metallicity can be well sustained in the van der Waals heterostructures even when the lattice mismatch goes beyond empirical wisdom around 1%. Considering the recent progress in fabricating the TMDCs MX$_2$ monolayers by peeling off a multilayer sample to a single layer [66, 67], we believe that the freestanding $h$-MnC monolayer can be further realized from the $h$-MnC/MoS$_2$ and $h$-MnC/MoSe$_2$ heterostructures by available exfoliation techniques. It is anticipated that our theoretical work will motivate experimental interests to synthesize such materials.
4. Conclusions

In conclusion, a graphene-like 2D $h$-MnC monolayer with unique electronic structure and robust ferromagnetic property has been systematically investigated by means of comprehensive first-principles calculations. According to the cohesive energy, phonon spectrum, elastic constant analyses, and AIMD simulations, the $h$-MnC monolayer clearly shows its structural, dynamical, mechanical, and thermal stability up to the temperature of 1000 K. The bonding type in the $h$-MnC monolayer can be described by Bader charge analysis that indicates a significant ionic character accompanied by the covalent component in some extent. The electronic structure reveals that the pristine $h$-MnC monolayer is predicted to be an intrinsic half-metal with robust ferromagnetism, exhibiting complete spin polarization, wide half-metallic gap of $E_g = 1.36$ eV near the Fermi energy level, large magnetic moment of 3 $\mu_B$ per unit cell, and sizable MAE as well. Estimated Curie temperature of 2D $h$-MnC crystal reaches around 200 K under $\pm 10\%$ external strain on the basis of the Heisenberg model MC simulations. Also, the $h$-MnC monolayer exposes its excellent half-metallic and ferromagnetic stabilities when applying biaxial in-plane strain ranging from $-6\%$ to $10\%$. The combination of these unique properties endows the $h$-MnC sheet a promising 2D material for the highly efficient application of next-generation paper-like spintronic devices. Furthermore, the realization of the freestanding $h$-MnC monolayer may well be prepared by exfoliation from its $h$-MnC/MoS$_2$ and $h$-MnC/MoSe$_2$ heterostructures that maintain the ferromagnetic state and half-metallic property. We hope that our theoretical work can provide justifications for follow-up experimental synthesis of the $h$-MnC monolayer and will inspire further researches to explore robust ferromagnetic and intrinsic half-metallic behaviors in many other novel materials in the measurable future.

Acknowledgments

This research was sponsored by the National Natural Science Foundation of China under Grant No. 11774041 and the Fundamental Research Funds for the Central Universities under Grant No. SWU019021.

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