Two-dimensional C\textsubscript{12}Mn\textsubscript{2}/C\textsubscript{12}Cr\textsubscript{2} as a room-temperature half metal/antiferromagnetic semiconductor: a systematic study†

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Ferromagnetism in half-metallic two-dimensional (2D) materials can lead to unique spintronics applications. In this paper, we report first-principle calculations that predict 2D single-layer C\textsubscript{12}Mn\textsubscript{2} as a ferromagnetic half metal, and 2D single-layer C\textsubscript{12}Cr\textsubscript{2} as an antiferromagnetic semiconductor. A systematic study is carried out to demonstrate the reliability of our research. We employ a bottom-up method to investigate the structural and magnetic stability of single, two and more Cr or Mn atoms on graphyne at room temperature. The very high Curie/Néel temperatures of 2D C\textsubscript{12}Mn\textsubscript{2}/C\textsubscript{12}Cr\textsubscript{2}, respectively, indicate the stability of room-temperature ferromagnetism/antiferromagnetism. With perfect spin filtering, 2D C\textsubscript{12}Mn\textsubscript{2} would be a promising material for future spintronics design.

1. Introduction

Spintronics is a promising field that employs electronic spin for data representation and storage. The information carrier of traditional electronic components such as diodes and transistors is electronic charge, but electronic spin is not considered. In spintronics logic devices, information processing is carried out by the controlled turning of electronic spin, with much lower energy consumption and higher data processing speed than traditional electronic devices. For example, a Datta–Das spin field-effect transistor exploits the Rashba spin–orbit interaction in a semiconductor to manipulate electronic spin and implement high-efficiency on/off control. However, one of the major difficulties is the low spin injection efficiency from ferromagnetic (FM) metal to semiconductor due to the great difference between their resistances. To solve this problem, people paid attention to magnetic semiconductors as a promising material to replace the metal–semiconductor junction. However, the development of a room-temperature magnetic semiconductor, whose preparation still suffers from low Curie temperature, is an outstanding conundrum in physics. Current diluted magnetic semiconductors, which are prepared by doping a magnetic transition metal (TM) element (e.g. Mn), have a Curie temperature of about 200 K.\textsuperscript{1–3} On the other hand, physicists have also considered antiferromagnetic (AFM) materials for nonvolatile spintronics data storage devices\textsuperscript{4} with advantages over conventional semiconductor devices. Antiferromagnets possess microscopic antiparallel arranged magnetic moments which are externally invisible with zero net magnetic moment. Therefore, information stored in antiferromagnets would be invisible to common magnetic probes and insensitive to disturbing magnetic fields.

Until now, more and more types of magnets have been put into practical applications. Further studies on new ferromagnets and antiferromagnets for spintronics applications are still needed to promote the development of spintronics.

Recently, two-dimensional (2D) materials such as graphene\textsuperscript{5–8} and MoS\textsubscript{2}\textsuperscript{9–11} have attracted much attention due to their ultra-thinness and extraordinary properties. The novel properties of 2D materials may open up a new way to achieve 2D ferromagnetism. Rycerz et al. suggested graphene as an adjustable material for valleytronics devices.\textsuperscript{12} FM silicene junctions were also proposed for spin- and valley-dependent transport applications.\textsuperscript{13} Kim et al. predicted a very large value of magnetoresistance in a graphene-nanoribbon-based field-effect transistor, which could be used as a spin valve.\textsuperscript{14–17} Recently, huge magnetoresistance was also found in zigzag silicene nanoribbons.\textsuperscript{18,19} However, these properties are highly dependent on the structure of zigzag edges, which unfortunately suffer from spontaneous reconstruction at room temperature.\textsuperscript{20–22} Moreover, a complicated chemical method has to be implemented for precisely fabricating graphene nanoribbons with a uniform width.\textsuperscript{23} The above disadvantages hinder the use of 2D material edges.

Achieving ferromagnetism inside 2D materials is always being pursued by scientists. Early on, graphene, \textit{i.e.} a semi-hydrogenated graphene sheet, was found to be an FM semiconductor.\textsuperscript{24} Then, people studied the possibility of engineering quantum anomalous/valley Hall states in graphene via TM atom binding.\textsuperscript{25} In practice, studies of magnetic low-dimensional...
semiconductor nanostructures have demonstrated that the confinement effect and the improved control of magnetic dopants can be used to increase the Curie temperature.26 Compared with graphene, semiconducting 2D materials might have different properties in magnetic modulations. Several decades ago, graphyne (GY) and its family (graphdiyne, graphyne-3 etc.) were predicted27–29 to be semiconductors with layered structures. From then on, much effort was devoted to their synthesis. Recently, large segments of graphyne and graphdiyne films have been successfully synthesized.30–34 Theoretical research has also been focused on the property modification of GY. In sp-hybridized C==C bonds of GY, the superposition of px and px±π* states could form orbitals towards any direction perpendicular to the C==C bond, leading to a possibility of bonding with TM atoms inside the GY surface, with a binding energy larger than graphene. In previous studies, it has been found that the 3d TM atoms on GY/graphdiyne not only efficiently modulate the electronic structures but also introduce unique magnetic properties for spintronics.35,36 To benefit the future development of 2D magnetic materials, further research on the reliability and feasibility of generating large-scale 2D magnetism by depositing TM atoms on GY is very necessary.

In this work, 2D single-layer C12Mn2/C12Cr2 are theoretically predicted as a half metal/antiferromagnetic semiconductor, respectively, and systematically studied using density functional theory (DFT) calculations. The ferromagnetism/antiferromagnetism of C12Mn2/C12Cr2 is proved to be stable at room temperature with very high Curie/Neél temperatures, respectively. We employ a bottom-up method to demonstrate the idea. First, we study the thermal stability of a single Cr or Mn atom on GY, proving that Cr or Mn atom aggregation at room temperature would be prevented by a high diffusion barrier. The spin-polarized carrier density of single Cr- or Mn-doped GY and their possible usage in spintronics is also explored. Second, Cr and Mn dimers in the GY surface are taken as theoretical models to study the magnetic coupling effect. Cr or Mn atoms in the GY surface are found to prefer separate locations (one atom in each acetylenic triangle), which provides an energetically favorable structure. Analysis of energy bands and carrier density reveals that the strong localization effect of Mn 3d orbitals leads to FM coupling, while more delocalized Cr 3d orbitals lead to AFM coupling. The Curie/Neél temperatures of Mn/Cr dimers, respectively, are found to be near room temperature, implying the possibility of forming a large-scale 2D magnetic layer. Finally, 2D hexagonal honeycomb lattices of C12Mn2/C12Cr2 are predicted to be FM/AFM with Curie/Neél temperatures of Tc = 1088 K/Tm = 749 K, respectively, indicating that their ferromagnetism/antiferromagnetism is very stable at room temperature. 2D C12Mn2 presents excellent half-metallic properties in a wide energy range near the Fermi level. We also systematically extended the study to 2D C12Fe2, C12Co2, C12Tc2 and C12Re2, finding AFM, FM, FM and AFM ground states with Tc = 26 K, Tm = 29 K, Tc = 247 K and Tm = 88 K, respectively. These Curie/Neél temperatures are all lower than those of C12Mn2/C12Cr2, and thus the ferromagnetism/antiferromagnetism of C12Co2 and C12Tc2/C12Fe2 and C12Re2 are less stable at room temperature. According to the study on energetics and thermal stability, 2D C12Mn2 might be easily prepared by Mn atomic deposition on GY. Overall, with perfect spin filtering, 2D single-layer C12Mn2 would be a promising material for spintronics. The results of this work may guide the future design of spintronics materials.

2. Theories and methods

Geometry relaxation and molecular dynamics (MD) simulations are performed within spin-polarized DFT and the generalized gradient approximation (GGA) of Perdew–Burke–Ernzerhof (PBE)37 by using a Vienna ab initio simulation (VASP) package.38,39 The projector-augmented wave method40,41 is used with a plane-wave energy cutoff of 400 eV. Grimme’s DFT-D2 correction42 is employed for evaluating dispersion interactions. The Hubbard U correction is employed to account for the correlation energy of the localized 3d orbital of TM atoms. The rotationally invariant formalism proposed by Dudarev et al. is used with Ueff = U − J instead of individual U and J values.43 Since the determination of Ueff via the linear-response method44 is time-consuming, we adopt the values Ueff = 3.55 and 5.01 eV for Cr and Mn, respectively, as reported by He et al.45 Single-layer GY with TM adatoms is simulated by a repeated slab model with (1 × 1) and (2 × 2) hexagonal supercells. The replicas of GY layers are separated by a vacuum layer of 15 Å in the direction perpendicular to the GY sheet. For (1 × 1) and (2 × 2) GY supercells, the Brillouin zone is sampled by using 4 × 4 × 1 and 2 × 2 × 1 Γ-centered Monkhorst-Pack grids, respectively. A Gaussian smearing with a width of σ = 0.05 eV is used. The convergence of the total energy is considered to be achieved when there are two iterated steps with an energy difference of less than 10−5 eV. To validate the above calculation method, we also tried a higher plane-wave energy cutoff (up to 650 eV) and the fluctuation of the average energy per atom was below 0.001 eV per atom. For spin states and magnetic moments, ref. 45 pointed out that the spin configurations of Cr and Mn adatoms are independent of the functional, and the results obtained by GGA+U are in good agreement with those obtained by the hybrid functional. For example, our calculated magnetic moments of the C12Cr2 unit cell obtained from PBE+U and the hybrid Heyd–Scuseria–Ernzerhof (HSE06) functional are 5.63 and 5.87 μB, respectively. To compare the magnetic moments, we also calculated other 3d TM adatoms on GY at the level of PBE+U (with Ueff from ref. 35) and HSE06, and then systematically extended the study to Fe, Co, Tc and Re (in Section 3.5) at the level of HSE06.

Geometries are fully relaxed without any symmetric constraints until the Hellmann–Feynman forces are below 0.01 eV Å−1. For geometry relaxations of FM and AFM states, to avoid being trapped in a local minimum, different initial magnetic moments are tested. MD simulations are performed using a Nosé thermostat. The Verlet algorithm is employed with a time step of 1 fs.

For total energy calculations and energy band plotting, the hybrid HSE06 functional46,47 was employed to account for exact electronic exchange. All the energy band calculations are performed using VASP with a plane-wave energy cutoff of 400 eV. For (1 × 1) and (2 × 2) GY supercells, we first perform self-consistent
calculations using $4\times4\times1$ and $2\times2\times1$ $\Gamma$-centered Monkhorst–Pack grids, respectively, and then carry out non-self-consistent calculations for 30 $k$-points sampled along the high symmetry line of the Brillouin zone. A Gaussian smearing with a width of $\sigma = 0.05$ eV is used.

To evaluate the stability of GY-TM configurations, we adopt the binding energy of a TM adatom on GY, which is defined as

$$E_b = E(GY) + E(TM) - E(GY-TM),$$

where $E(GY)$, $E(TM)$ and $E(GY-TM)$ denote the total energies of free-standing GY, free TM adatom and the GY-TM system, respectively. To find the minimum-energy path (MEP) and the corresponding potential barrier $E_0$ for metal adatom diffusion and catalytic reactions, the climbing image nudged elastic band (CINEB) method was used. Seven images were inserted in between two stable states, and the spring constant between adjacent images was 0.1 eV Å$^{-1}$. Based on the calculated barriers $E_0$, the typical time scale of the process could be estimated from the Arrhenius law

$$\tau = \omega^{-1} \exp(E_0/kT).$$

where $k$ is the Boltzmann constant and $T$ is the temperature. The empirical parameter $\omega \approx 10^{13}$ s$^{-1}$ roughly corresponds to the average vibration frequency of chemical bonds. All the binding energy and potential barrier calculations are performed using the VASP package.

To quantify the transport ability and spin polarization of carriers, density of states (DOS), carrier concentration and spin polarizability are evaluated. In the conduction bands, the electron concentration reads

$$n = \frac{1}{A} \int_{E < CBM} \frac{D(E)dE}{e^{(E-E_F)/kT} + 1}$$

with the integral over the energy $E$ above the conduction band minimum (CBM). Here, $D(E)$ denotes the DOS at energy $E$, $E_F$ denotes the Fermi energy, $T$ denotes the temperature, and $A$ denotes the area of the 2D unit cell. In the valence bands, the hole concentration reads

$$p = \frac{1}{A} \int_{E < VBM} \frac{D(E)dE}{1 - e^{(E-E_F)/kT} + 1}$$

with the integral over the energy $E$ below the valence band minimum (VBM). The spin polarizability at the energy $E$ reads

$$P(E) = \frac{|D_\uparrow(E) - D_\downarrow(E)|}{D_\uparrow(E) + D_\downarrow(E)},$$

where $D_\uparrow(E)$ and $D_\downarrow(E)$ are the spin-up and spin-down part of DOS, respectively. For conductors, the conductance mainly depends on the electrons near the Fermi level, and thus the spin polarizability of electric currents through the conductor depends on $D_\uparrow(E_F)$ and $D_\downarrow(E_F)$.

The stability of FM systems is predicted by evaluating the Curie temperature. According to the Heisenberg model, the exchange energy of a set of spins in a lattice reads

$$E_{ex} = -J_1 \sum_{1st} \mathbf{S}_i \cdot \mathbf{S}_j - J_2 \sum_{2nd} \mathbf{S}_i \cdot \mathbf{S}_j - J_3 \sum_{3rd} \mathbf{S}_i \cdot \mathbf{S}_j - \cdots,$$

where the summations are taken over the nearest neighbors, 2nd-nearest neighbors, 3rd-nearest neighbors, etc. and $J_i > 0$ are the corresponding couplings between spins. For two spin-$S$ atoms coupled in FM or AFM state, we have $(\mathbf{S}_i \cdot \mathbf{S}_j)_{\text{FM}} = S^2$ or $(\mathbf{S}_i \cdot \mathbf{S}_j)_{\text{AFM}} = -S(S+1)$, respectively. For a lattice with $N$ spin-$S$ atoms in FM state, $\mathbf{S}_i \mathbf{S}_j = S^2$ holds for every spin pair. For a lattice in AFM state, $\mathbf{S}_i \mathbf{S}_j = S(S+1)$ holds for the 1st-, 3rd-nearest neighbors, etc. and $\mathbf{S}_i \mathbf{S}_j = S^2$ holds for the 2nd-, 4th-nearest neighbors, etc. So, the total energy difference between FM and AFM states reads

$$E(\text{AFM}) - E(\text{FM}) = J_1 \sum_{1st} (\mathbf{S}_i \cdot \mathbf{S}_j)_{\text{AFM}} - J_2 \sum_{2nd} (\mathbf{S}_i \cdot \mathbf{S}_j)_{\text{AFM}} - J_3 \sum_{3rd} (\mathbf{S}_i \cdot \mathbf{S}_j)_{\text{AFM}} - \cdots$$

$$+ J_2 \sum_{2nd} (\mathbf{S}_i \cdot \mathbf{S}_j)_{\text{FM}} + J_3 \sum_{3rd} (\mathbf{S}_i \cdot \mathbf{S}_j)_{\text{FM}} + \cdots$$

$$= N(z_1 J_1 + z_2 J_3 + \cdots)S(S+1),$$

where $z$ is the number of nearest neighbors. According to the mean-field theory, the Curie temperature reads

$$T_c = \frac{2(z_1 J_1 + z_2 J_3 + \cdots)S(S+1)}{3k}$$

$$= \frac{2(E(\text{AFM}) - E(\text{FM}))(S+1)/3N(2S+1)}{k}. (7)$$

The systems with the coupling $J_i < 0$ have AFM ground states, and would transform into paramagnetic states (PM) at high temperature. According to the mean-field theory, the Néel temperature for the AFM-PM transformation reads

$$T_n = \frac{2(z_1 J_1 + z_2 J_3 + \cdots)S(S+1)}{3k}$$

$$= \frac{2(E(\text{FM}) - E(\text{AFM}))(S+1)/3N(2S+1)}{k}. (8)$$

3. Results and discussion

3.1 Basic information

Before going to our results, we first present the structure of free-standing GY. The primitive cell of GY (enclosed by dashed lines in Fig. 1(a)) contains 12 C atoms. The optimized lattice constant $a = 6.89$ Å is in very good agreement with ref. 53. As shown in Fig. 1(a), the C–C bond length in the hexagon is $1.42$ Å, and the C–C bond lengths in the acetylenic linkages are 1.41 and 1.22 Å (with a deviation of less than 1% relative to the values in ref. 54 and 55). The calculated band gap 0.48/0.98 eV at the level of PBE/HSE06, respectively, is in good agreement with ref. 53–57.

To understand the bonding between GY and TM atoms, we take a $(2 \times 2)$ GY supercell as the simulation model. As shown in Fig. 1(a), the center (C) site in the acetylenic triangle, the hollow (H) site in the center of the hexagonal ring, and B1 and B2 as two bridge sites on C–C bonds are considered. According to total energy calculations, the C site is the most stable site with the lowest binding energy for all 3d TM atoms. This result is in agreement with ref. 35. Then, to identify the ground states of GY-TM systems, we study both the spin-polarized FM state and the non-spin-polarized non-magnetic (NM) state of single
3.2 Thermal stability

In thermal motion, a single Cr/Mn atom bound on GY may migrate in two ways. The first way is leaving the GY surface in thermal motion. The second way is migrating from one C site to another. For the thermal motion of a Cr/Mn atom leaving the GY surface, we plotted the MEP and potential barrier using the CINEB method and found that the process is barrierless, i.e., the total energy increases with enlarging Cr/Mn-GY distance. Hence the barrier for a Cr/Mn atom leaving the GY surface is just equivalent to the binding energy \( E_b \), and the typical time scale of the process should be decided by the binding energy \( E_b \) of Cr/Mn on GY. According to the calculations, the binding energy of a single Cr/Mn atom on a \((2 \times 2)\) GY supercell is \( E_b = 1.48/1.30 \) eV at the level of PBE+U and \( E_b = 1.82/1.84 \) eV at the level of HSE06, respectively (Table 1). According to the Arrhenius law (eqn (3)), at \( T = 300 \) K the time scale for the event of a Cr/Mn atom leaving the GY surface is \( \tau = \omega^{-1} \exp(E_b/kT) = 1.2 \times 10^{10}/2.6 \times 10^{10} \) years (using the \( E_b \) values at the level of HSE06), respectively. This result suggests that the Cr/Mn atom could be stably bound on the C site, without leaving the GY surface at room temperature. It is worth noting that the binding energy of Cr/Mn on graphene is larger than that on graphene, so GY could be a promising substrate for a Cr/Mn atom.

For the thermal diffusion of a TM atom on the GY surface, two possible paths are considered. The first path (Fig. 1(b)) is migration from one C site to a neighboring C site via climbing over the C–C acetylenic bond (i.e., the unstable B2 site). The second path (Fig. 1(b)) is migration from one C site to another C site via the H site. According to our calculations, the energy of Cr/Mn on the H site is found to be higher than that on the B2 site. From the point of view of thermodynamics, the first path with lower energy should be more probable than the second one. So, we calculate the MEP and potential barrier of the first path using the CINEB method. For a Cr/Mn atom, the calculated barrier is \( E_b(C \rightarrow C) = 0.64/0.60 \) eV at the level of PBE+U and \( E_b(C \rightarrow C) = 0.92/1.15 \) eV at the level of HSE06. According to the Arrhenius law (eqn (3)), at \( T = 300 \) K the time scale for the C–C diffusion of a Cr/Mn atom is \( 2.9 \times 10^{10}/2.1 \times 10^6 \) s (using the \( E_b(C \rightarrow C) \) values at the level of HSE06), respectively. This result indicates that the diffusion of a Cr/Mn atom is hindered by the barrier, prohibiting Cr/Mn atom aggregation at room temperature. In addition, the dimerization of two Cr/Mn atoms on GY is tested. The total energy of a Cr/Mn dimer on the C site is found to be higher than the total energy of two separated Cr/Mn atoms on GY. In the view of energetics, Cr/Mn atoms on the GY surface prefer staying on different C sites. To further prove the above results, we carry out MD simulations for two Cr/Mn atoms located on neighboring C sites. After running at \( T = 800 \) K with a duration of 1500 fs, the geometry is still retained without Cr/Mn atom aggregation.

### Table 1: The binding energy \( E_b \) of single Cr/Mn atom on a \((2 \times 2)\) GY supercell and the magnetic moment \( \mu \) (in \( \mu_B \)) of the GY-Cr/GY-Mn system. The diffusion barrier \( E_b(C \rightarrow C) \) of a single Cr/Mn atom migrating from one C site to another is also given. All the values on the left/right of slash are calculated at the level of PBE+U/HSE06, respectively.

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<tr>
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<th>( E_b ) (eV)</th>
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<td>Cr</td>
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<td>4.58/4.50</td>
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<td>Mn</td>
<td>1.30/1.84</td>
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Fig. 1  (a) Atomic configuration of free-standing GY sheet. The primitive cell is enclosed by dashed lines. The C–C bond lengths (in Å) are indicated. C, H, B1 and B2 are considered binding sites for TM adatoms. (b) A schematic of Cr/Mn atom diffusion from one C site to another, with energy profile and the barrier \( E_0(C \rightarrow C) \) shown.

atoms on a \((2 \times 2)\) GY supercell. For every 3d TM atom, the total energy of the FM state is found to be lower than that of the NM state. In the C site, the 3d orbitals of the TM atom are split by the ligand field of the surrounding C skeleton with \( D_{3h} \) symmetry, leading to possible spin polarization. In the region of intermediate interaction (ligand splitting is close to exchange splitting), among 3d TM atoms the largest magnetic moments would occur for Cr and Mn. Among 3d TM atoms, Cr/Mn are found to have the largest magnetic moments of 4.58/3.96 \( \mu_B \) at the level of PBE+U and 4.50/4.00 \( \mu_B \) at the level of HSE06, respectively (Table 1). The PBE+U values are larger than the PBE values in ref. 58. With the largest magnetic moments (similar to Cr/Mn on graphene), Cr and Mn on GY are selected as the objects of study in this paper.
Overall, the single-layer GY sheet should be a favorable substrate for separating Cr/Mn atoms.

3.3 Single Cr/Mn atom on GY

We study the basic physics, starting from a single Cr/Mn atom bound on a \((2 \times 2)\) GY supercell (corresponding to doping concentration of about 2%). In the most stable C site, the Cr/Mn atom is surrounded by C–C acetylenic bonds with trigonal symmetry (Fig. 2(a)). To analyze the effect of C–C bonds, the partial density of states (PDOS) is projected onto the 3d orbitals of the Cr/Mn atom and the 2p\(\pi\) orbitals of C–C bonds. In Fig. 2(b), we can see that the 3d orbitals of Mn are highly spin-polarized, with spin-up states much more occupied than spin-down states. The nearby C atoms are then influenced, with the 2p\(\pi\) orbitals partially spin-polarized. At energies of \(-5.9\), \(-3.8\) and \(-2.8\) eV below the Fermi level (red, blue and gray arrows in Fig. 2(b), respectively), we can find peak values of PDOS for C 2p\(\pi\), Mn 3d\(x^2\) + 3d\(y^2\) and Mn 3d\(xy\) + 3d\(x^2-y^2\), which indicate the covalent feature of bonding between C 2p\(\pi\) and Mn 3d orbitals.

The energy bands of GY\( (2 \times 2)\)-Cr and GY\( (2 \times 2)\)-Mn are plotted in Fig. 2(c) to make a comparison with pure \((2 \times 2)\) GY. Note that in \((1 \times 1)\) GY the band gap locates at the \(M\) point, but in \((2 \times 2)\) GY the band gap is folded into the \(\Gamma\) point. GY has semiconductor features with a direct band gap of 0.98 eV at the level of HSE06. At \(T = 300\) K, the carrier concentration in GY is \(c = n + p = 9.4 \times 10^{10}\) cm\(^{-2}\) (Table 2). For GY\( (2 \times 2)\)-Cr and GY\( (2 \times 2)\)-Mn, the energy bands all show highly spin-polarized
conductor features, with the Fermi level through the conduction bands (the 2nd and 3rd panels in Fig. 2(c)). At $T = 300$ K, the carrier concentration of $\text{GY}(2 \times 2)$-Cr/$\text{GY}(2 \times 2)$-Mn is $c \approx n = 7.2 \times 10^{13}/6.9 \times 10^{13}$ cm$^{-2}$ (much higher than that of graphene $(10^{11}$-10$^{12}$ cm$^{-2}$)), respectively (Table 2). For $\text{GY}(2 \times 2)$-Cr, direct band gaps of 0.40/0.59 eV below the conduction bands are found for spin-up/spin-down bands, respectively. For $\text{GY}(2 \times 2)$-Mn, direct band gaps of 0.60/0.63 eV below the conduction bands are found for spin-up/spin-down bands, respectively.

The energy-dependent spin polarizability $P(E)$ (eqn (5)) of $\text{GY}(2 \times 2)$-Cr and $\text{GY}(2 \times 2)$-Mn is plotted in Fig. 2(d). For $\text{GY}(2 \times 2)$-Cr, it can be seen that the electrons/holes in the valence/conduction bands, respectively, both have high spin polarizability. At the Fermi level, the spin polarizability $P(E_F)$ is 30%, which leads to spin-polarized current through $\text{GY}(2 \times 2)$-Cr under bias voltage.

At VBM ($-0.73$ eV below the Fermi level), the spin polarizability is even close to 100%, which implies a potential use of Cr-doped GY in spintronics. By applying an appropriate gate voltage (i.e. > 0.73 V), we might lower the Fermi level to under VBM, inducing hole conductance with very high spin polarization in Cr-doped GY.

However, the spin polarizability in the conduction bands of $\text{GY}(2 \times 2)$-Mn is rather low (the lower panel in Fig. 2(d)). At the Fermi level of $\text{GY}(2 \times 2)$-Mn, the spin polarizability $P(E_F)$ is only 4%. This limits the direct usage of Mn-doped GY in spintronics applications. Fortunately, the spin polarizability in the valence bands is higher than in the conduction bands, with a maximum of 30% at VBM ($-0.85$ eV). So, like Cr-doped GY, we might also realize spin-polarized hole conductance by applying an appropriate gate voltage (i.e. > 0.85 V) to lower the Fermi level of Mn-doped GY to under VBM.

Overall, Cr- and Mn-doped GY both show spin polarization features in electronic transport, with high spin polarization at VBM. The above results indicate the potential usage of Cr- and Mn-doped GY as electrically controllable materials for spintronics. Furthermore, we might increase the doping concentration of Cr/Mn atoms to enhance their magnetism and spin polarizability. The feasibility will be studied in the following section.

### 3.4 AFM/FM coupling between neighboring Cr/Mn atoms

In spintronics applications, the materials used should have stable magnetism, with energetically favorable FM coupling between magnetic sites. To explore the possibility of FM coupling between Cr/Mn atoms on GY, we employ the simulation model in Fig. 3(a), with two TM atoms located on adjacent C sites of a $\text{GY}(2 \times 2)$ supercell. For geometry relaxations of FM and AFM states, to avoid being trapped in a local minimum, different initial magnetic moments are tested. According to the results, the FM configuration of $\text{GY}(2 \times 2)$-Mn$_2$ is more energetically stable than the AFM configuration ($E_{\text{AFM}} - E_{\text{FM}} > 0$) (the binding energies of Mn are $E_b = 1.93/1.87$ eV per atom (at the level of HSE06) for the FM/AFM configuration, respectively). While the FM configuration of $\text{GY}(2 \times 2)$-Cr$_2$ is more energetically unstable than the AFM configuration ($E_{\text{AFM}} - E_{\text{FM}} < 0$) (the binding energies of Cr are $E_b = 1.67/1.72$ eV per atom (at the level of HSE06) for the FM/AFM configuration, respectively). This result has been demonstrated by both PBE+U and HSE06 calculations. Table 3 displays the magnetic moment $\mu$ (FM) and the total energy difference $E_{\text{AFM}} - E_{\text{FM}}$ between the FM and AFM configurations of FM $\text{GY}(2 \times 2)$-Cr$_2$ and $\text{GY}(2 \times 2)$-Mn$_2$ systems at the level of HSE06. The above results suggest the possibility of ferromagnetism in a large GY sheet with dense Mn doping. For FM $\text{GY}(2 \times 2)$-Cr$_2$/GY$(2 \times 2)$-Mn$_2$, their total magnetic moments 8.52/6.51 $\mu_B$ (Table 3), respectively, are a bit less than two times those of GY$(2 \times 2)$-Cr/GY$(2 \times 2)$-Mn (9.00/8.00 $\mu_B$). In the GY$(2 \times 2)$-Cr$_2$ lattices, the nearest/2nd-nearest neighbor distances of Cr atoms are 3.96/10.54 Å, respectively. In the GY$(2 \times 2)$-Mn$_2$ lattices, the nearest/2nd-nearest neighbor distances of Cr atoms are 3.87/10.61 Å, respectively. Since the 2nd-nearest neighbor distance is longer than the 1st-nearest neighbor distance, the 1st-nearest neighbor couplings should dominate the magnetic exchange interactions.

To predict the stability of the FM GY$(2 \times 2)$-Mn$_2$ system, the Heisenberg model is employed to estimate the Curie temperature $T_C$ (eqn (6) and (7)). According to the magnetic moment of FM GY$(2 \times 2)$-Mn$_2$ (6.51 $\mu_B$), we can roughly estimate a spin of $S = 3/2$ for each Mn atom. With the Mn atom number $N = 2$ and $E_{\text{AFM}} - E_{\text{FM}} = 0.11$ eV, we have $zJ_{1} + zJ_{2} + \cdots = 9.2$ meV (eqn (6)) and the Curie temperature $T_C = 267$ K (eqn (7) and Table 3). Such a $T_C$ near room temperature implies the possibility of room-temperature ferromagnetism in a GY sheet with a higher Mn doping concentration. In contrast, the GY$(2 \times 2)$-Cr$_2$ system is found to have an AFM ground state. With $N = 2$ and $E_{\text{AFM}} - E_{\text{FM}} = -0.11$ eV, we have $zJ_{1} + zJ_{2} + \cdots = -9.2$ meV (eqn (6)).

The calculated Néel temperature for the AFM-PM transformation is $T_N = 267$ K (eqn (8) and Table 3).

The energy bands of AFM GY$(2 \times 2)$-Cr$_2$ are plotted in the left panel of Fig. 3(b), showing typical features with the Fermi level through the conduction bands. At $T = 300$ K, the carrier concentration of AFM GY$(2 \times 2)$-Cr$_2$ is $c = 1.3 \times 10^{14}$ cm$^{-2}$ (Table 2), which is about twice that of the carrier concentration of GY$(2 \times 2)$-Cr. This result indicates that the electrons contributed by the Cr atoms are nearly free electrons. In contrast, the carrier concentration of FM GY$(2 \times 2)$-Mn$_2$ $c = 6.5 \times 10^{13}$ cm$^{-2}$ (Table 2) is even a little lower than that of GY$(2 \times 2)$-Mn $(6.1 \times 10^{13}$ cm$^{-2}$). We infer that this result might reveal the strongly localized features of Mn 3d electrons. In the energy bands of FM GY$(2 \times 2)$-Mn$_2$ (right panel of Fig. 3(b)), we can see that the CBM is located at $-0.15$ eV below the Fermi level, which is more shallow than the CBM of GY$(2 \times 2)$-Mn $(at -0.25$ eV below the Fermi level). Two nearly flat bands can be found at about $-1.6$ eV below the Fermi level, which generally

<table>
<thead>
<tr>
<th>$p$ (cm$^{-2}$)</th>
<th>$n$ (cm$^{-2}$)</th>
<th>$c = n + p$ (cm$^{-2}$)</th>
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<tr>
<td>4.7 \times 10^8</td>
<td>4.7 \times 10^9</td>
<td>9.4 \times 10^8</td>
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<td>$\text{GY}(2 \times 2)$-Cr</td>
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<td>7.2 \times 10^{13}</td>
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<tr>
<td>$\text{GY}(2 \times 2)$-Mn</td>
<td>0</td>
<td>6.9 \times 10^{13}</td>
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<tr>
<td>FM GY$(2 \times 2)$-Mn$_2$</td>
<td>0</td>
<td>6.5 \times 10^{13}</td>
</tr>
</tbody>
</table>

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correspond to strongly localized states with small overlaps between the replicas of supercells. The above results imply that neighboring Mn atoms could strongly bind electrons, forming localized states with high spin polarization. The energy bands in the GY sheet are affected and then spin-polarized. It can be seen that the spin-up VBM of FM GY(2 × 2)-Mn2 (−0.65 eV) is 0.14 eV higher than the spin-down VBM (−0.79 eV), leading to 100% spin polarization near the spin-up VBM (Fig. 3(c)). At the Fermi level of FM GY(2 × 2)-Mn2, the spin polarization is about 9%, which is about two times the value for GY(2 × 2)-Mn.

3.5 2D magnetic materials: C12Cr2 and C12Mn2

Based on the above results, we further considered the maximum TM atom embedding in the GY surface. Since neighboring Cr/Mn atoms tend to AFM/FM coupling, respectively, it can be inferred that maximum antiferromagnetism/ferromagnetism would be realized with one Cr/Mn atom embedded in every C site (in the center of the acetylenic triangle) of GY (see the upper pane in Fig. 4(a)). We performed geometry relaxation on this structure as the initial configuration, and then found a deformation of the original structure. The optimized structures are shown in the lower part of Fig. 4(a), in which the Cr/Mn atom bonds with three C atoms in the acetylenic triangle and strongly draws them, changing the C-TM system into a 2D honeycomb structure with buckling. To check the result, we used a 2 × 2 GY supercell with a Cr/Mn atom embedded in every C site, and the geometry relaxation still yielded the same structure. The new-found 2D honeycomb structures can be presented by the chemical constitutions C12Cr2 and C12Mn2, with their rhombic primitive cells shown in Fig. 4(a). The ground states of

![Fig. 3](image-url) — (a) A sketch of a GY(2 × 2) supercell with two TM atoms located on adjacent C sites. The unit cell is enclosed by dashed lines. (b) Band structures of AFM GY(2 × 2)-Cr2 and FM GY(2 × 2)-Mn2. The solid (red)/dashed (blue) lines present the spin-up/spin-down channels, respectively. (c) The spin polarizability P of FM GY(2 × 2)-Mn2. The Fermi level is set to zero. The calculations are all performed at the level of HSE06.

![Table 3](table-url) — The 1st column shows the ground states of GY(2 × 2)-Cr2/(2 × 2)-Mn2. The 2nd column shows the total energy difference E(AFM) − E(FM) between the AFM and FM states of GY(2 × 2)-Cr2/(2 × 2)-Mn2. The 3rd column shows the binding energies E_b (per atom) of Cr and Mn adatoms. The 4th column shows the magnetic moment \( \mu_{(FM)} \) of FM GY(2 × 2)-Cr2 and GY(2 × 2)-Mn2. The 5th column shows the Curie/Neél temperature for FM/AFM ground state, respectively. The calculations are performed at the level of HSE06.

<table>
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<tr>
<th>Ground state</th>
<th>( E_{(AFM)} - E_{(FM)} ) (eV)</th>
<th>( E_b ) (eV per atom)</th>
<th>( \mu_{(FM)} ) (( \mu_B ))</th>
<th>Curie/Neél temperature</th>
</tr>
</thead>
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<tr>
<td>GY(2 × 2)-Cr2 AFM</td>
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<td>1.67</td>
<td>1.72</td>
<td>8.52</td>
</tr>
<tr>
<td>GY(2 × 2)-Mn2 FM</td>
<td>0.11</td>
<td>1.93</td>
<td>1.87</td>
<td>6.51</td>
</tr>
</tbody>
</table>
C\textsubscript{12}Cr\textsubscript{2}/C\textsubscript{12}Mn\textsubscript{2} are found to be AFM/FM, coincident with GY(2\times 2)-Cr\textsubscript{2}/GY(2\times 2)-Mn\textsubscript{2}, respectively. The lattice constants of C\textsubscript{12}Cr\textsubscript{2}/C\textsubscript{12}Mn\textsubscript{2} are \(a_0 = 6.89/6.92\) Å, respectively (Table 4). In the AFM C\textsubscript{12}Cr\textsubscript{2}/FM C\textsubscript{12}Mn\textsubscript{2} lattice, the binding energy of Cr/Mn is 1.76/1.56 eV per atom at the level of HSE06, respectively, which is close to the binding energy in GY(2\times 2)-Cr/GY(2\times 2)-Mn and GY(2\times 2)-Cr\textsubscript{2}/GY(2\times 2)-Mn\textsubscript{2}. To further prove the thermal stability of 2D C\textsubscript{12}Cr\textsubscript{2} and C\textsubscript{12}Mn\textsubscript{2}, we carry out MD simulations at \(T = 800\) K with a duration of 3000 fs. As an example, Fig. 4(c) shows the changes in temperature, and the bond lengths between the Mn atom and the three nearest C atoms in the MD simulation of a 2D C\textsubscript{12}Mn\textsubscript{2} sheet. We can see that the temperature and the bond lengths keep in a certain range throughout the simulation. After the running of the simulation, the geometries of single-layer C\textsubscript{12}Cr\textsubscript{2} and C\textsubscript{12}Mn\textsubscript{2} are still retained, suggesting that C\textsubscript{12}Cr\textsubscript{2} and C\textsubscript{12}Mn\textsubscript{2} sheets are stable.

The right panel in Fig. 4(b) plots the energy bands of single-layer FM C\textsubscript{12}Mn\textsubscript{2}, showing obvious half-metallic features with high spin polarization. The electrons are fully spin-polarized in the range of \(-0.77--0.14\) eV near the Fermi level. The unit cell of FM C\textsubscript{12}Mn\textsubscript{2} has a magnetic moment of 6.04 \(\mu_B\). We can roughly estimate a spin of \(S = 3/2\) for each Mn atom. The energy difference between AFM and FM unit cells (with Mn atom number \(N = 2\)) is \(E_{\text{AFM}} - E_{\text{FM}} = 0.45\) eV (Table 4). Here, we consider the relativistic spin-orbital coupling (SOC). It is worth noting that for C\textsubscript{12}Cr\textsubscript{2} and C\textsubscript{12}Mn\textsubscript{2} the influence of SOC

![Figure 4](https://example.com/fig4.png)

**Fig. 4** (a) The top and side view of AFM C\textsubscript{12}Cr\textsubscript{2} and FM C\textsubscript{12}Mn\textsubscript{2}. The upper pane presents the original structure before geometry relaxation, in which one Cr/Mn atom is embedded in every C site (in the center of the acetylenic triangle) of GY. Lattice vectors and rhombic cells are shown by arrows and dashed lines. The lattice constant is denoted by \(a_0\). (b) Band structures of AFM C\textsubscript{12}Cr\textsubscript{2} and FM C\textsubscript{12}Mn\textsubscript{2}. The solid (red)/dashed (blue) lines present the spin-up/spin-down channels, respectively. (c) Changes of temperature and the bond lengths between the Mn atom and the three nearest C atoms obtained from MD simulation of the FM C\textsubscript{12}Mn\textsubscript{2} sheet. The calculations of (a) and (b) are performed at the level of HSE06. The calculations of (c) are performed at the level of PBE+U.
on total energy is less than 1%. According to the Heisenberg model, the coupling constant is estimated to be $z_1J_1 + z_3J_3 + \cdots = 37.5$ meV (eqn (6)), corresponding to the Curie temperature $T_c = 1088$ K (eqn (7)). Such a high $T_c$ indicates that the ferromagnetism of $C_{12}$Mn$_2$ is very tenacious against temperature, leading to stable magnetism at room temperature. As we have demonstrated that the structure of $C_{12}$Mn$_2$ (with an Mn atom separated in each binding site) is energetically favorable, 2D FM $C_{12}$Mn$_2$ might be easily prepared by depositing Mn atoms on the GY surface. This conclusion would benefit future development of spintronics.

In contrast, single-layer $C_{12}$Cr$_2$ shows AFM features. The right panel in Fig. 4(a) plots the energy bands of single-layer AFM $C_{12}$Cr$_2$, showing a semiconducting feature with an indirect band gap of 0.96 eV. The energy difference between AFM and FM unit cells is $E_{\text{AFM}} - E_{\text{FM}} = -0.31$ eV (Table 4). With the Cr atom number $N = 2$, the coupling constant is estimated to be $z_1J_1 + z_3J_3 + \cdots = 25.8$ meV, and the Heisenberg model predicts a Néel temperature of $T_n = 749$ K for the AFM-PM transformation (eqn (8)). Such a high $T_n$ indicates that $C_{12}$Cr$_2$ is a stable 2D AFM material at room temperature.

To make a comparison, we also consider single-layer $C_{12}$Fe$_2$/C$_{12}$Co$_2$, but find that their ferromagnetism/antiferromagnetism could only be retained at very low temperature. $C_{12}$Fe$_2$ and $C_{12}$Co$_2$ both have honeycomb structures. The ground state of $C_{12}$Fe$_2$ is AFM, with lattice constant $a_0 = 6.95$ Å and $E_{\text{AFM}} - E_{\text{FM}} = 0.01$ eV (Table 4). The Néel temperature is $T_n = 26$ K. In contrast, the ground state of $C_{12}$Co$_2$ is found to be FM with lattice constant $a_0 = 6.94$ Å and $E_{\text{AFM}} - E_{\text{FM}} = 0.01$ eV (Table 4). The Curie temperature is calculated to be $T_c = 26$ K. Since the Néel/Curie temperatures of single-layer $C_{12}$Fe$_2$/C$_{12}$Co$_2$, respectively, are very low, $C_{12}$Fe$_2$ and $C_{12}$Co$_2$ should be conventional 2D PM materials at room temperature.

Since $C_{12}$Mn$_2$ is successful in forming a 2D half metal, we then consider other Mn group elements, i.e. Tc and Re. For $C_{12}$Tc$_2$ and $C_{12}$Re$_2$, SOC is taken into account. According to the results, 2D $C_{12}$Tc$_2$ and $C_{12}$Re$_2$ are also honeycomb lattices. The ground state of $C_{12}$Tc$_2$ is FM with lattice constant $a_0 = 6.78$ Å and $E_{\text{AFM}} - E_{\text{FM}} = 0.09$ eV (Table 4). 2D $C_{12}$Tc$_2$ shows halfmetallic features with the electrons fully spin-polarized in the range of $-0.46$ to $-0.46$ eV near the Fermi level. However, the Curie temperature $T_c = 247$ K below room temperature would hinder the practical application of 2D $C_{12}$Tc$_2$ in spintronics. The ground state of $C_{12}$Re$_2$ is even AFM with lattice constant $a_0 = 6.81$ Å and $E_{\text{AFM}} - E_{\text{FM}} = -0.03$ eV (Table 4). The very low Néel temperature $T_n = 88$ K makes 2D $C_{12}$Re$_2$ PM at room temperature.

4. Conclusions

In conclusion, 2D single-layer FM/AFM materials $C_{12}$Mn$_2$/C$_{12}$Cr$_2$, respectively, are theoretically predicted to be tenacious against temperature, with high Curie/Néel temperatures of 1088/749 K. These results indicate that single-layer $C_{12}$Mn$_2$/C$_{12}$Cr$_2$ could remain FM/AFM at room temperature. We use a bottom-up method to demonstrate this idea, employing DFT calculations at the level of hybrid functional HSE06. First, a single Cr or Mn atom is proved to be stable in the GY surface, with the center of the acetylene triangle as the most stable binding site. The binding energy and diffusion barrier are high enough to prevent Cr or Mn atom aggregation at room temperature. The Cr or Mn atom prefers to be located in different center sites, which is energetically favorable and advantageous to separate Cr or Mn atom in the GY surface. Second, the magnetic coupling between neighboring Cr or Mn atoms in the GY surface are studied to preliminarily investigate the possibility of large-scale magnetism by Cr or Mn atoms in GY. An Mn dimer in the GY surface is found to be FM with Curie temperature $T_c = 267$ K, while a Cr dimer in the GY surface is found to be AFM with Néel temperature $T_n = 267$ K. The $T_c/T_n$ of the Mn/ Cr dimers, respectively, near room temperature reveal the possibility of forming a large-scale 2D magnetic layer. Finally, 2D hexagonal honeycomb lattices of $C_{12}$Mn$_2$/C$_{12}$Cr$_2$ are predicted to be FM/AFM with Curie/Néel temperatures $T_c = 1088$ K/$T_n = 749$ K, respectively, indicating that their ferromagnetism/antiferromagnetism are very stable at room temperature. The 2D single-layer $C_{12}$Mn$_2$ shows half-metallic features with full spin polarization. In addition, we also investigate single-layer $C_{12}$Fe$_2$/C$_{12}$Co$_2$, finding very low Curie/Néel temperatures, respectively, which limits their usage in spintronics. Overall, as a 2D FM half-metal, single-layer $C_{12}$Mn$_2$ would be a promising 2D material. The above result might benefit the future development of spintronics devices.

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References


temperature in (Ga,Mn)As, Appl. Phys. Lett., 2008, 93, 132103.


