Theoretical Understanding of Magnetic and Electronic Structures of Ti_3C_2 Monolayer and Its Derivatives

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Abstract

First-principles calculations were performed to investigate the electronic and magnetic properties of Ti_3C_2 monolayer and its derivatives. We found that pristine Ti_3C_2 monolayer acts as a magnetic metal, and magnetic moments come from Ti^{2+} ions at two sides. Through doping nitrogen atoms, the spin moments is significantly reduced. On other hand, when two surfaces of Ti_3C_2 monolayer are saturated by external groups, the magnetism will be spontaneously annihilated. Even for the saturation of one side, we also found that the magnetism of $\text{Ti}_3\text{C}_2\text{Y}$ (Y is O and OH) monolayer is removed because of the invalidation of stoner instability. More importantly, we explored that both doping and surface modification will reduce the Curie temperature of Ti_3C_2 monolayer. Therefore, our results shed a light on the way to get high-temperature magnetism in Ti_3C_2 monolayer.

Because of the flat and large surface of two-dimensional (2D) atomic crystals, 2D materials typically exhibit physical and chemical properties that differ from those of 3D bulk counterparts. Due to such excellent properties, graphene and similar materials have well been taken as the next-generation electric devices^[1-2]. However, it has been well demonstrated that the most widely studied 2D nano-materials, such as graphene, hexagonal BN sheet, and transition metal dichalcogenide^[3-5], do not have spin-polarized states which will block their practical application in spintronic devices.

To obtain the room-temperature magnetic 2D nanomaterials, a lot of works have been reported in the past decades. Ugeda *et al.* experimentally explored that vacancy can create local magnetic moments in graphene⁶, and Pisani *et al.* suggested that such created magnetic moments can interact with each other through ferromagnetic coupling⁷. But the magnetic coupling strongly depends on defect concentration. Doping transition metal (TM) into the lattice of boron nitride monolayer or graphene like material to get the ferromagnetic state was also proposed by Krasheninnikov *et al.* and Wei *et al.*^[8-9] Since the doped TMs themselves are intrinsically magnetic, their participations in the graphene like system may create required magnetism. However, it is still difficult to realize the uniform doping without forming clusters or secondary phase^[10-13]. In recent years, we have proposed several ways to realize the ferromagnetism in two-dimensional materials^[14-16]. For example, we have proposed that the ferromagnetic half-metallicity can be produced in the dimethylmethylen-bridged triphenylamine (DTPA) porous sheet¹⁵, and wurtzite MnO thin films can automatically create graphene-like magnetic materials^[16]. Normally, it is well known that the TM atoms can contribute to macroscopic magnetism, as explored in organometallic porous sheets or 2D MnPSe₃ nanosheet.^[17-18] Consequently, searching 2D TM-based materials may provide us the highly desired room-temperature ferromagnetism.

Recently, a large family of 2D material named MXenes has attracted a lot of interests because of their excellent electrical conductivities, chemical stability, and hydrophilic surfaces. Mxenes are produced by selectively etching the “A” metal from M_{n+1}AX_n (n=1, 2, 3) or MAX phases, where M represents an early transition metal, A

corresponds to IIIA or IVA group elements, and X is C or N.^[19] Over 60 MAX phases have been demonstrated in experiments. Some researcher have revealed that MXenes and their some derivations are desirable materials for high-performance anodes of Li-ion batteries due to their high Li-ion storage capacities.^[20-22] Moreover, the MXene also provide the possible ways for hydrogen storage, supercapacitors, and environmental pollutant decontamination.^[23-27]

Figure 1 Optimized Geometries of the Free-standing Ti_3C_2 and Ti_3CN . Green balls are Ti atoms, gray balls are carbon atoms, and blue balls are nitrogen atoms.

To date, the most studied Mxene is Ti_3C_2 (Ti_3CN) produced by the room temperature (RT) exfoliation of Ti_3AlC_2 in hydrofluoric acid. Zhou *et al.* and Xie *et al.* theoretically predicted that the Ti_3C_2 monolayer is ferromagnetic.^[20-21] However, the ferromagnetic property is not observed or confirmed in the experiments. By carefully looking back the whole experimental details, we found a lot of chemical groups may be introduced on the surface of Ti_3C_2 monolayer, which has been well explored in experiments^[28-29]. Herein, it is important to explore the role of such chemical groups on the magnetic property, and find a way to realize the ordered spin structures. In the present work, we performed first-principles calculation based on density functional theory (DFT) method to systematically investigate the electronic and magnetic property of the Ti_3C_2 and Ti_3CN monolayer influenced by the surface modification.

Our first-principles calculations were based on spin-polarized density functional theory (DFT) method within the generalized gradient approximation (GGA) as implemented in the *Vienna ab initio simulation package* (VASP) code.^[30] A 500 eV

cutoff was used for the plane-wave basis set. For the exchange-correlation energy, the Perdew, Burke, and Ernzerhof (PBE) functional is used for our research.^[31] The projected augmented wave (PAW) method with a plane-wave basis set was used for the ion-electron interaction.^[32-33] For the spin-polarized calculations, the Vosko-Wilk-Nusair modification scheme was applied to interpolate the correlation energy.^[34] In order to investigate the magnetic interactions, a $2 \times 2 \times 1$ supercell is adopted. All of the structures were relaxed using the conjugated gradient method, and the convergence criterions were set to be 10^{-4} eV in energy and 10^{-3} eV/Å in force. The Brillouin zone was represented by Monkhorst-Pack special K-point mesh^[35] of $8 \times 8 \times 1$ during the geometry optimization, while a $21 \times 21 \times 1$ K-point is used for electronic structure calculations.

Figure 2. Calculated band dispersions for (a) Ti_3C_2 monolayer and (b) Ti_3CN monolayer. Orange circles mean up-spin channel, and violet circles mean down-spin channel. (c) Plotted spin density for pristine Ti_3C_2 (left) and Ti_3CN monolayer (right).

In addition to Ti_3C_2 monolayer, the electronic and magnetic calculations on Ti_3CN monolayer, in which one layer of C atoms is substituted by N atoms, are also carried out. According to the atomic environment, there are two different Ti atoms labelled as Ti_1 (on the surface) and Ti_2 (in the middle) for Ti_3C_2 monolayer respectively (As displayed in Figure 1). Through the further substitution of N atoms, the chemical

environment of two Ti_1 sides has been changed, which lead to different Ti_1 atoms.

We first calculated the ferromagnetic state of Ti_3C_2 and Ti_3CN monolayer, which has been predicted as the ground states in previous reports. As plotted in Figure 2a, the plotted band dispersion shows that both Ti_3C_2 and Ti_3CN monolayer are metallic in two spin channels. Besides, we also noticed that only the states around Fermi level (roughly 2 eV) show the observable spin splitting. Compared with Ti_3C_2 monolayer, the plotted spin density of Ti_3CN monolayer is largely reduced. This means that electron doping will reduce the spin moment, and lower the stability of magnetism. Furthermore, the calculated magnetic moments come from the superficial Ti_1 ions, while the Ti_2 ions in the middle are nonmagnetic. Since outside Ti atoms are not saturated, it is expected that they will create local states, and lead to spin moments. Consequently, doping electrons will saturate such states, and annihilate the spin structures.

From the above studies, we know that the ferromagnetism is stemming from the superficial Ti atoms. Since Mxenes are produced by selectively etching the “A” metal, the external groups, such as F, H, O and OH, cannot be avoided in practical process. So what will happen if the superficial Ti atoms are saturated with such functional groups? In the following part, the investigations on the electronic and magnetic properties of the Ti_3C_2 monolayer superficially doping with F, H, O and OH on both sides or one side are presented.

Figure 3. a) both sides of Ti_3C_2 monolayer are saturated by external groups; (b) Plotted partial DOS of d orbitals for Ti atoms in pristine FM Ti_3C_2 monolayer. (c) Plotted DOS of d_{z^2} , d_{xz} and

dyz orbitals of Ti atoms under external groups. P means pristine monolayer, and H, F, OH, O means saturating two sides with such chemical groups.

When the two sides of Ti_3C_2 monolayer are saturated by the external groups, namely, F, H, O and OH, we found that all the cases are non-spin-polarized solutions. As shown in Figure 3b, spin moments of Ti_3C_2 monolayer are mainly distributed in dz^2 , dxz and dyz orbitals. To see the origin of magnetic annihilation, we plotted the density of states (DOS) of such orbitals. As shown in Figure 3c, without any saturation, a large amount of states distributes around Fermi Level. Consequently, stoner instability will lead to spin-polarized states. However, by saturation, such states have been removed from the Fermi level, and make the whole systems non-magnetic.

Figure 4. (Top) Plotted spin density of Ti_3C_2 monolayer with single side saturation of H atoms. (Bottom) Plotted DOS of dz^2 , dxz and dyz orbitals of Ti atoms in Ti_3C_2 monolayer with single side saturation of OH groups.

For the case of unilateral doping, the FTi_3C_2 and HTi_3C_2 monolayers are magnetic metals while the OTi_3C_2 and OHTi_3C_2 monolayer are still NM. Even for the magnetic FTi_3C_2 and HTi_3C_2 monolayer, we also found that the spin moments have been greatly reduced (Figure 4). Similar with the above discussion, we plotted the partial DOS of dz^2 , dxz and dyz orbitals of OHTi_3C_2 monolayer in Figure 4. It is clear that peak of plotted orbitals has been shifted away from Fermi Level, which is also

explored in the case of OTi₃C₂ monolayer. Therefore, no spin-polarized state is stabilized.

In order to explore how the chemical modification affects the spin interaction, and predict the Curie temperature of such monolayers, it is crucial to examine their possible spin exchange paths. J₁ is the intra-layer interaction and J₂ is the inter-layer interaction between the top and bottom layers. To determine the values of J₁ and J₂ on the basis of DFT calculations, we calculate the total energies of the three ordered spin states Ti₃C₂ and its derivations depicted in Figure 5. The relative energies per formula unit (FU) of the three ordered spin states obtain from DFT calculations are summarized in Table 1. The total spin exchange interaction energies of these states can be expressed in terms of the spin Hamiltonian

$$\hat{H} = -\sum_{i<j} J_{ij} \hat{S}_i \cdot \hat{S}_j$$

in which J_{ij} is the exchange parameter for the interaction between the spin sites *i* and *j*, while S_i and S_j are the spin angular momentum operators at the spin sites *i* and *j*, respectively. When the energy expressions obtained for spin dimmers with N unpaired spins per spin site are applied (in the present case, N= 2),^[36-37] the total spin-exchange energies (per formula unit) of the three ordered spin states are written as

$$E_{FM} = (-48J_1 - 24J_2)N^2 / 16$$

$$E_{AF2} = (16J_1 + 8J_2)N^2 / 16$$

$$E_{AF3} = (-48J_1 + 24J_2)N^2 / 16$$

Thus, the values of J₁ and J₂ listed in Table 2 are determined by equating the relative energies of the three ordered spin states obtained from DFT calculations to the corresponding relative energies obtained from the total spin exchange energies. The J₁ is of superexchange (SE) type involving Ti₁-C-Ti₁ paths, while the J₂ is of the supersuper-exchange (SSE) type involving Ti₁-C...C-Ti₁ paths.^[38-39] Our calculations show that J₁ is FM and J₂ is AFM for Ti₃C₂ monolayer. However, the Ti₃C₂ monolayer

is overall FM due to the strength of J_1 is stronger than J_2 . With the altering the atomic environment, the spin exchange interactions are correspondingly changed in the case of Ti_3CN monolayer. J_1 and J_2 are both of FM but the strength of J_1 is much stronger than J_2 . In the case of unilateral doping, the FTi_3C_2 and HTi_3C_2 monolayer, the spin exchange interactions J_1 and J_2 of FTi_3C_2 and HTi_3C_2 monolayer are also listed in Table 2 for comparing with the values of Ti_3C_2 monolayer. It can be seen that the J_1 are always FM. Moreover, we also found the magnetic through surface modification, the dominated spin interaction, namely, J_1 , in all cases, has been significantly weakened.

Figure 5. Three ordered spin states of Ti_3C_2 monolayer employed to extract the spin exchanges J_1 and J_2 . The unshaded and shaded circles represent the Ti_1^{2+} ions with up-spin and down-spin, respectively.

With the calculated exchange parameter J_1 , we performed Monte Carlo simulations to estimate the Curie temperature for the FM order^{16, 40}. To obtain T_c , we first calculate the specific heat, and TN can be obtained by locating the peak position in the specific heat vs T plot, shown in Figure 6. In our simulation, we use the 20×20 two-dimensional lattices (Our test shows that larger lattice gives similar T_c). From the simulated specific heat curve (Figure 6), we find that the chemical doping or surface modification will lower down the Curie temperature.

In summary, based on Density Functional Theory (DFT) method based on the first-principle calculation, we systematically investigate the electronic and magnetic properties of Ti_3C_2 monolayer and its derivations. In analysis of the PDOS of Ti_3C_2 , our calculation predicts that the Ti_3C_2 monolayer is ferromagnetic metal and the magnetic origin is from the superficial Ti_1 ion while the Ti_2 ion in the middle is nonmagnetic. Similar results are also explored for Ti_3CN monolayer. Once two

surfaces are saturated with external groups, spontaneous magnetism of Ti_3C_2 monolayer will be removed. When only one side is saturated, we found that magnetism can survive for F and H modified Ti_3C_2 monolayer. Furthermore, through evaluating the spin interaction, we demonstrate that all the spin interaction is weakened after doping/chemical modification, compared with that of pristine Ti_3C_2 monolayer, which is also confirmed by the simulated Curie temperature. Therefore, our results explore that clean surfaces are the necessary condition to gain strong magnetism in Ti_3C_2 monolayer.

Figure 6 The simulated X-T curve for Ti_3C_2 monolayer and its derivatives (X: Specific heat).

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Table 1: Relative Energies (in meV) of the Three Ordered Spin States Obtained from DFT calculations.

Magnetic	FM	AFM1	AFM2
Ti ₃ C ₂	0	70.49	-42.23
Ti ₃ CN	0	40.69	9.30
FTi ₃ C ₂	0	47.79	0
HTi ₃ C ₂	0	45.79	53.41

Table 2: Spin-Exchange Parameters J₁-J₂ (in meV) Obtained from DFT Calculations

	J ₁	J ₂
Ti ₃ C ₂	6.17	-3.52
Ti ₃ CN	2.15	0.78
FTi ₃ C ₂	2.99	0
HTi ₃ C ₂	0.64	4.45

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