Two-dimensional Ti$_2$C monolayer (MXene): surface functionalization, induced metal, semiconductor transition

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Abstract: Recently, two-dimensional (2D) transition metal carbides and nitrides known as MXenes, have gained a lot of attention because of their tunable electronic and magnetic properties depending on surface functionalization. In the present work, the structural, electronic, and magnetic properties of both T and H phases of bare Ti$_2$C and fully surface terminated Ti$_2$CT$_2$ (T = -F, = O, -OH) are calculated using a set of first principles calculations. The ground state structures of Ti$_2$CT$_2$ are computed in two and four different configurations for both H and T phases, respectively. We demonstrate that while H phase of Ti$_2$C exhibits half-metallic behavior with magnetic moments of 2 $\mu_B$ per formula unit, it displays metallic behavior with magnetic moments of 1.27 $\mu_B$, 0.25 $\mu_B$ per formula unit, and semiconductor behavior with 0.35 eV band gap in -F, -OH, and =O surface functionalization, respectively. We also show that while T phase of Ti$_2$C exhibits metallic behavior with magnetic moment of 1.89 $\mu_B$ per formula unit, it stays in metallic nonmagnetic behavior in both -F and -OH. Meanwhile, it displays semiconductor behavior with 0.25 eV band gap in -O surface functionalization. We expect that our results can advance the future applications of MXenes from energy storage to spintronic.

Key words: 2D materials, density functional theory, MXenes, Ti$_2$C, electronic and magnetic properties, surface functionalization

1. Introduction
Two-dimensional (2D) freestanding materials show unique properties that differ from those of their conventional bulk (3D) precursors because they lack a degree of freedom. The first 2D material, graphene, was discovered in 2004 by mechanical exfoliation method [1, 2]. This method is the most economical way to achieve single layer material. The alternative of 2D materials [3–6], such as hexagonal BN [7], transition metal oxides [8] and transition metal dichalcogenides (TMDs) [9, 10] have also been synthesized by the same method. Naguib et al. reported that they obtained a compose of a few Ti$_3$C$_2$ layers and canonical scrolls produced by exfoliation of Ti$_3$AlC$_2$ in hydrofluoric acid [11] at room temperature. These new 2D materials occur when Al atoms are extracted from Ti$_3$AlC$_2$, which was proposed to be called “MXene” to emphasize its graphene-like morphology. MXenes has just recently entered the research area as a new member of 2D materials family. Their general formula consist of M$_{n+1}$AX$_n$ (n=1,2,3), M, A, and X represent early transition metal, A-group elements, and C and/or N, respectively. They were produced by selectively etching "A" layers out of the MAX bulk. After their exfoliation from the MAX phase, MXenes are fully surface-terminated by functionalized groups.

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After the synthesis of Ti$_3$C$_2$, almost 30 MXenes have been also experimentally discovered, and dozens have been theoretically predicted [12–15]. The exfoliation process of MAX phases is still the main challenge of getting 2D monolayer MXenes. Lei et al. considered three different structures which are monolayer alpha-Mo$_2$C, 1T-Mo$_2$C, and 2H-Mo$_2$C [16]. Their calculations indicate that 2H-Mo$_2$C is determined to be energetically most favorable among these three. To our knowledge, they put forward the physical and thermal properties of 2H-Mo$_2$C in the literature for the first time. Motivated by the study, we investigated the electronic and magnetic properties of bare Ti$_2$C and fully surface terminated Ti$_2$CT$_2$ for both H and T phases.

Surface functionalization is a critical issue on electronic, magnetic, and their tunable properties of MXenes. There are several studies that can be cited as examples: Champagne et al. [17] investigated electronic properties and dynamical stabilities, both bare V$_2$C and fully surface terminated V$_2$CT$_2$ from first-principles calculations. They showed that pristine V$_2$C shows metallic behavior and keeps its metallic behavior in all surface groups. Si et al. [18] showed intrinsic half-metallicity in bare Cr$_2$C due to mobility of d electrons of Cr atoms. They also showed a ferromagnetic-antiferromagnetic transition which stems from surface functionalization groups (F, OH, H, or Cl), band gap of the semiconductor can be controlled by changing the type of functional groups. The effect of surface functionalization groups was also investigated by Zhang et al. [19]. They reported that surface functionalization groups are crucially important considering their unsaturated surface which allows electron-phonon interaction.

2. Computational methodology

The structural, electronic, and magnetic properties of all the considered systems were performed by first-principles calculations using density functional theory (DFT), as implemented in the Vienna ab initio simulation package (VASP) code [20, 21]. The exchange-correlation potential energies were described by the generalized gradient approximation (GGA) [22] of Perdew-Burke-Ernzerhof (PBE) [23] functional. The density functional theory (DFT), D2 method for Grimme, was used for the GGA function with van der Waals (vdW) correction [24].

After testing of significant input parameters, structural calculations were performed by using the following parameters: The energy cutoff value for plane-wave basis set was taken to be 600 eV. The total energy was minimized until the energy between consecutive steps in the iterations variation was less than 10$^{-5}$ eV. Hellmann–Feynman force convergence criterion was taken to be 10$^{-5}$ eV. Fermi level Gaussian smearing factor was taken as 0.05 eV. 16 × 16 × 1 k-point grid in Γ-centered mesh for the primitive unit cell was selected for the Brillouin zone (BZ) integration. The vacuum spacing was selected 20 Å between two adjacent layers to avoid interactions between the periodic images of slabs in the z-direction. Ti, C, F, O, and H atoms were treated as 3s$^2$3p$^6$3d$^3$4s$^1$, 2s$^2$2p$^2$, 2s$^2$2p$^5$, 2s$^2$2p$^4$, and 1s$^1$ as valence electrons, respectively.

3. Results

3.1. Structural properties

We started with fully relaxed geometry optimization of pristine H phase Ti$_2$C. The ground state structure of pristine H phase Ti$_2$C is found to be hexagonal crystal structure as shown in Figure 1a. a = b = 3.05 Å are found as equilibrium lattice parameters. To our knowledge, there is no report of performing the structural properties of H phase Ti$_2$C. After we got ground-state crystal structure of pristine Ti$_2$C, we continued functionalization
of Ti$_2$C MXene structure with T = F, O, OH. We considered two different configurations of functional groups for H phases: functionalized groups stay at the top site of Ti and C atoms shown respectively in Figures 1b and 1c. Structural parameters and formation energies of these structures are given in Table 1.

![Figure 1](image)

**Figure 1.** Systematic illustration of H phases of (a) pristine Ti$_2$C and surface terminated functionalization Ti$_2$CT$_2$ MXene systems: top and side views of (b) MD - I and (c) MD - II, respectively. Titanium, carbon, and functional groups represented in blue, brown, and red, respectively.

Formation energies are calculated to get the most stable configuration using the following formula:

$$\Delta H_f = E_{tot}(\text{Ti}_2\text{CT}_2) - E_{tot}(\text{Ti}_2\text{C}) - E_{tot}(T_2),$$

(1)

where $E_{tot}(\text{Ti}_2\text{CT}_2)$, $E_{tot}(\text{Ti}_2\text{C})$, $E_{tot}(T_2)$ total energy of fully surface terminated Ti$_2$CT$_2$, total energy of pristine Ti$_2$C and total energy of F$_2$, O$_2$ or (OH)$_2$, respectively. MXenes surfaces are assumed that there were no remaining bond as pending [25]. The structural parameters and calculated formation energy are reported in Tables 1 and 2.
Table 1. Structural parameters and formation energies for unterminated $H$-$Ti_2C$ and surface chemically functionalized systems called MD-I and MD-II.

<table>
<thead>
<tr>
<th></th>
<th>Model</th>
<th>Lattice Parameter $a$ (Å)</th>
<th>Thickness $d$ (Å)</th>
<th>Magnetic moment $(\mu_B)$</th>
<th>Formation Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H$-$Ti_2C$</td>
<td>MD-I</td>
<td>3.10</td>
<td>2.59</td>
<td>1.73</td>
<td>–11.21</td>
</tr>
<tr>
<td></td>
<td>MD-II</td>
<td>2.95</td>
<td>2.65</td>
<td>1.27</td>
<td>–13.40</td>
</tr>
<tr>
<td>$H$-$Ti_2CF_2$</td>
<td>MD-I</td>
<td>3.28</td>
<td>2.41</td>
<td>0.00</td>
<td>–11.22</td>
</tr>
<tr>
<td></td>
<td>MD-II</td>
<td>2.96</td>
<td>2.89</td>
<td>0.00</td>
<td>–15.23</td>
</tr>
<tr>
<td>$H$-$Ti_2CO_2$</td>
<td>MD-I</td>
<td>3.12</td>
<td>2.585</td>
<td>1.33</td>
<td>–8.31</td>
</tr>
<tr>
<td></td>
<td>MD-II</td>
<td>3.00</td>
<td>2.58</td>
<td>0.25</td>
<td>–11.00</td>
</tr>
</tbody>
</table>

We used the same method in the computation of $T$ phase Ti$_2$C for calculating fully relaxed geometry optimization as in the computation of $H$ phase Ti$_2$C. The ground-state structure of pristine $T$ phase Ti$_2$C is also found to be hexagonal as shown in Figure 2a. The unit cell includes three atoms; two titanium and one carbon are located at $(1/3, 2/3, z)$, $(2/3, 1/3, -z)$, and $(0, 0, 0)$ on the Wyckoff sites. A, A’, and B sites was selected fcc and hcp sites located on the top of Ti atom and fcc site located on the top of C atom, respectively. The equilibrium lattice parameters for $T$ phase Ti$_2$C is found $a = b = 3.08$ Å. The lattice parameter of $T$ phase Ti$_2$C is also verified by the previous studies; $a = 3.083$ Å [26] and $a = 3.078$ Å [27]. Our results show that while lattice parameters decreases, Ti-Ti atomic distance (thickness) increases. After we got ground-state crystal structure of pristine $T$ phase Ti$_2$C, we continued functionalizing Ti$_2$C MXene structure with $T = F$, $O$, OH. To determine the ground state for $T$ phase Ti$_2$CT$^2$, we calculated formation energies with Equation 1 in all functional groups which are listed in Table 2. Functionalization configurations are created according to the position of surface groups. We introduced four configuration models. In model MD-I, two functionalized groups are located on the top of the Ti atoms as shown in Figure 2b. In model MD-II, two functionalized groups are positioned on the top of A hollow site as shown in Figure 2c while one functionalized group is positioned on the top of A hollow site and second functionalized same type on the top of B hollow site in model MD-III as shown in Figure 2d. Finally, in model MD-IV, two functionalized groups are positioned on the top of hollow site B as shown in Figure 2e.

As seen in Tables 1 and 2, MD-II and MD-III configurations have the lowest formation energy for $H$ and $T$ phases, respectively. Total energies of $H$ and $T$ phases are found as –24.20 eV and –25.39 eV per unit cell. Clearly, $T$ phase of Ti$_2$C is the most stable. The structural stability of the $H$ and $T$ phases was estimated by comparing their relative total energies. Clearly, relative total energy is 1.19 eV per unit cell and $H$-$T$ phase transition may possible. Further studies are needed to confirm this and it should be investigated deeply.

3.2. Electronic and magnetic properties

Having determined the ground-state structures of $H$ and $T$ phases of pristine Ti$_2$C monolayers (MD-II and MD-III were selected as ground-state for $H$ and $T$ phases, respectively) we focused on electronic and magnetic properties. Bare MXenes show metallic character with high density of states because of transition metal atoms have d- bonding near the Fermi level. Passivated from F, O, OH functional groups, the electronic properties may change dramatically. All calculated electronic band structures are given along the high symmetry direction as $\Gamma$, M, K.
Figure 2. Systematic illustration of T phases of (a) bare Ti$_2$C and fully terminated functionalization Ti$_2$CT$_2$ MXene systems: top and side views of (b) MD-I, (c) MD-II, (d) MD-III, and (e) MD-IV, respectively. Titanium, carbon, and functional groups represented in blue, brown, and red, respectively.

Table 2. Structural parameters and formation energies of MD-I–MDIV configurations for pristine T-Ti$_2$C and chemically functionalized systems.

<table>
<thead>
<tr>
<th>Model</th>
<th>Model</th>
<th>Lattice Parameter (a) (Å)</th>
<th>Thickness (\text{d}) (Å)</th>
<th>Magnetic moment (\text{M}_B)</th>
<th>Formation Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(T)-Ti$_2$C</td>
<td></td>
<td>3.08</td>
<td>2.24</td>
<td>1.89</td>
<td>0</td>
</tr>
<tr>
<td>(T)-Ti$_2$CF$_2$</td>
<td>MD-I</td>
<td>3.19</td>
<td>2.19</td>
<td>0.00</td>
<td>–12.01</td>
</tr>
<tr>
<td></td>
<td>MD-II</td>
<td>2.97</td>
<td>2.43</td>
<td>0.03</td>
<td>–13.27</td>
</tr>
<tr>
<td></td>
<td>MD-III</td>
<td>3.05</td>
<td>2.29</td>
<td>0.07</td>
<td>–13.83</td>
</tr>
<tr>
<td></td>
<td>MD-IV</td>
<td>3.02</td>
<td>2.35</td>
<td>0.00</td>
<td>–13.61</td>
</tr>
<tr>
<td>(T)-Ti$_2$CO$_2$</td>
<td>MD-I</td>
<td>3.03</td>
<td>2.62</td>
<td>0.00</td>
<td>–16.14</td>
</tr>
<tr>
<td></td>
<td>MD-II</td>
<td>2.96</td>
<td>2.77</td>
<td>0.00</td>
<td>–14.37</td>
</tr>
<tr>
<td></td>
<td>MD-III</td>
<td>3.03</td>
<td>2.62</td>
<td>0.00</td>
<td>–16.16</td>
</tr>
<tr>
<td></td>
<td>MD-IV</td>
<td>3.01</td>
<td>2.67</td>
<td>0.00</td>
<td>–15.38</td>
</tr>
<tr>
<td>(T)-Ti$_2$C(OH)$_2$</td>
<td>MD-I</td>
<td>3.22</td>
<td>2.17</td>
<td>0.00</td>
<td>–9.05</td>
</tr>
<tr>
<td></td>
<td>MD-II</td>
<td>3.01</td>
<td>2.41</td>
<td>0.00</td>
<td>–10.87</td>
</tr>
<tr>
<td></td>
<td>MD-III</td>
<td>3.06</td>
<td>2.32</td>
<td>0.00</td>
<td>–11.21</td>
</tr>
<tr>
<td></td>
<td>MD-IV</td>
<td>3.05</td>
<td>2.35</td>
<td>0.00</td>
<td>–11.07</td>
</tr>
</tbody>
</table>

\(H\) phase of pristine Ti$_2$C shows half-metallic behavior magnetic moments of 2 \(\mu_B\) per formula unit in Figure 3a. Terminated Ti$_2$CT$_2$ \((T = F, OH)\), each F or OH group obtains one electron from Ti$_2$C turn to metallic character with magnetic moments of 1.27 \(\mu_B\) and 0.25 \(\mu_B\) per formula unit, respectively as shown in
Figures 3b and 3d. Oxygen surface termination changes metallic to semiconductor with 0.35 eV band gap value as shown in Figure 3c.

We also investigated T phase of pristine Ti$_2$C that indicates metallicity with magnetic moments of 1.89 \( \mu_B \) per formula unit in Figure 4a. We have also tested the magnetic moment and is also verified by the previous studies; 1.91 \( \mu_B \) per formula unit \cite{26}. F and OH functional group passivations do not change metallic behavior. Magnetic moment of 1.89 \( \mu_B \) per formula unit vanished when passivated with F and OH. It basically turns to nonmagnetic metallic. Like H phase of pristine Ti$_2$C, O passivated T phase of pristine Ti$_2$C changed its electronic properties to semiconductor with 0.25 eV.

![Figure 3](image-url)

Figure 3. Spin-resolved band structure of H phases of pristine (a) Ti$_2$C and fully terminated functionalization Ti$_2$CT$_2$ as (b) Ti$_2$F$_2$ (c) Ti$_2$O$_2$ and (d) Ti$_2$(OH)$_2$ at the equilibrium lattice constants.

4. Summary and concluding remarks

We theoretically investigated the structural, electronic and magnetic properties of both H and T phases of Ti$_2$C (MXene). We showed for the first time in the literature that Ti$_2$C changes from being half-metallic to metallic, or to semiconductor in the H phase and being metallic to semiconductor in the T phase, upon surface functionalization. Transition from metal to semiconductor and metal to half-metal in both H and T phases of Ti$_2$C (MXene) would be interesting issue 2D materials beyond graphene. Nonmagnetic MXenes are also strong candidates for superconductivity due to their display of metallic character.
Figure 4. Spin-resolved band structure of T phases of pristine (a) Ti$_2$C and fully terminated functionalization Ti$_2$CT$_2$ as (b) Ti$_2$F$_2$ (c) Ti$_2$O$_2$ and (d) Ti$_2$(OH)$_2$ at the equilibrium lattice constants.

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