Hybrid Density Functional Study of Structural and Electronic Properties of Functionalized Ti_{n+1}X_n (X= C, N) monolayers

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Abstract

Density functional theory simulations with conventional (PBE) and hybrid (HSE06) functionals were performed to investigate the structural and electronic properties of MXene monolayers, Ti_{n+1}C_n and Ti_{n+1}N_n (n = 1–9) with surfaces terminated by O, F, H, and OH groups. We find that PBE and HSE06 give similar results. Without functional groups, MXenes have magnetically ordered ground states. All the studied materials are metallic except for Ti_2CO_2, which we predict to be semiconducting. The calculated density of states at the Fermi level of the thicker MXenes (n \geq 5) is much higher than for thin MXenes, indicating that properties such as electronic conductivity and surface chemistry will be different. In general, the carbides and nitrides behave differently with the same functional groups.

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I. INTRODUCTION

The study of two-dimensional (2D) materials is a topic of current interest, not only for their unique properties\textsuperscript{1-3} compared with their three-dimensional (3D) counterparts, but also for their important applications to industry and engineering\textsuperscript{4-7}. Over the years, despite many experimental efforts on 2D materials, only a few classes of freestanding single-layer 2D materials have been successfully synthesized. Among them, the very first and most fascinating one is graphene\textsuperscript{1} which is prepared from exfoliated graphite. Other graphene-like materials, such as hexagonal BN and dichalcogenides, are synthesized by exfoliation of their 3D-layered precursors\textsuperscript{8-10}. Normally, these compounds are considered as van der Waals solids due to the weak interaction between layers, making them able to be exfoliated. Alternatively, the synthesis of freestanding 2D monolayers from 3D-layered solids with strong interlayer bonds is more difficult.

Very recently, a new family of 2D materials was prepared by the exfoliation of the layered ternary transition metal carbides, which are known as MAX phase\textsuperscript{11,12}. The latter is a large family of layered solids, including ternary transition metal carbides, nitrides, and carbonitrides, with more than 70 members. The MAX phases usually possess unique properties, such as remarkable machinability, high damage tolerance, excellent oxidation resistance, and high electrical and thermal conductivity, with various industrial applications\textsuperscript{13-15}. These solids have a general formula of $M_{n+1}AX_n$ ($n = 1, 2, 3, \cdots$), where “M” is an early transition metal, “A” represents the main group elements (mostly group IIIA and IVA), and “X” denotes C and/or N. MAX phases adopt hexagonal structures (space group $P6_3/mmc$), and their structures can be viewed as inter-growth structures consisting of hexagonal $M_{n+1}X_n$ layers and planar A atomic sheets with alternative stacking along the $c$ direction. The crystal structure of $M_3AX_2$ is shown in Fig. 1(a) as an example. In general, the MAX phases are quite stable. However, compared to the strong M–X intralayer bonds, the interatomic A–A bonds and interlayer M–A bonds are weaker, making A atomic layers chemically more reactive. In turn, taking $Ti_3AlC_2$ as an example, the Al layers can be extracted from the solid $Ti_3AlC_2$ by hydrofluoric acid treatment and sonication, resulting in graphene-like $Ti_3C_2$ nanosheets, so-called “MXene”\textsuperscript{16}. Depending on the synthesis conditions, the surfaces of $Ti_3C_2$ monolayers are chemically terminated with oxygen-containing and/or fluoride groups. Following the same procedure, other MXenes, including $Ti_2C$, $Ta_4C_3$, $Ti_3CN$, \textit{etc.}
(Ti_{0.5}Nb_{0.5})_2C, and (Ti_{0.5}Cr_{0.5})_2C, have been prepared by exfoliation of the corresponding carbides and carbonitrides. Notably, due to the large number of MAX family, it is predictable that more MXenes will be synthesized by exfoliation of their corresponding MAX phases.

Several studies have been conducted to understand the properties of these newly discovered graphene-like MXenes. It has been shown that these materials are good electrical conductors and have high elastic moduli. The intercalation of Li ion and organic molecules into Ti_2C, Ti_3C_2, Ti_3CN, and TiNbC sheets suggests they are promising candidates for Li-ion battery anodes and hybrid electrochemical capacitors. And with proper termination groups, the functionalized MXenes could become semiconductors with large Seebeck coefficients as potential thermoelectric materials. However, up to now these studies are mainly focused on the M_2X and M_3X_2 type of MXenes, there are no reports on the properties of exfoliated carbides or nitrides with other n.
In this work, we investigate systematically the evolution of structural and electronic properties of graphene-like titanium carbide and nitride MXenes (Ti$_{n+1}$C$_n$ and Ti$_{n+1}$N$_n$, $n = 1$–9) with different functional groups (F, O, H, and OH) using conventional and hybrid density functional calculations. We show that all the studied materials are metals except for Ti$_2$CO$_2$. With the same surface termination, carbides and nitrides exhibit different electronic properties. The density of states (DOS) at the Fermi level increases in both carbides and nitrides with distinct trends, as $n$ increases. Moreover, the calculations suggest that the “pure” carbide and nitride monolayers are magnetic. After functionalization, magnetism is removed.

II. COMPUTATIONAL DETAILS

The first principle calculations are carried out using density functional theory (DFT) as implemented in the Vienna ab initio simulation package (VASP)\textsuperscript{27}. The all-electron projected argument wave (PAW) method\textsuperscript{28} is used to describe the ion–electron interaction, with 1$s^1$, 2$s^22p^2$, 2$s^22p^3$, 2$s^22p^4$, 3$s^23p^3$, and 3$d^24$s^2 treated as valence electrons for H, C, N, O, F, Al, and Ti, respectively. For Ti, PAW configurations including 3$s$ and/or 3$p$ electrons in the valence give the similar results. For the exchange-correlation energy, we use both the Perdew–Burke–Ernzerhof (PBE) version of generalized gradient approximation (GGA)\textsuperscript{29} and the Heyd–Scuseria–Ernzerhof (HSE06)\textsuperscript{30–32} hybrid functional. The latter can be described through the following equation:

$$E_{xc}^{HSE} = \frac{1}{4}E_{x}^{HF,SR}(\mu) + \frac{3}{4}E_{x}^{PBE,SR}(\mu) + E_{x}^{PBE,LR}(\mu) + E_{c}^{PBE}.$$  \hfill (1)

The PBE exchange term is split into a short range (sr) and a long-range (lr) part. Then, 25$\%$ of short range part is replaced by a short range Hartree–Fock term. The correlation part of PBE is not changed. The screening parameter in HSE was fixed at a value of 0.2 Å$^{-1}$. This functional obtains improved formation energies and more reliable band gaps than PBE\textsuperscript{30,33} and is therefore better able to identify stable structures and the metallic or insulating character of the MXenes.

A plane wave cutoff energy of 580 eV is sufficient to ensure the convergency of total energies to 1 meV per primitive cell. The underlying structural optimization are performed using the conjugated gradient method, and the convergency criterion was set to $10^{-6}$ eV/cell.
FIG. 2. (color online) Structure configurations of functionalized MXenes with different arrangements of the surface atoms: side views of (a) I–Ti$_4$X$_3$T$_2$, (b) II–Ti$_4$X$_3$T$_2$, and (c) III–Ti$_4$X$_3$T$_2$; (d) and (e) top views of I–Ti$_4$X$_3$T$_2$ and II–Ti$_4$X$_3$T$_2$. Since configuration III is a mixture of I and II, the top view of III is not shown.

in energy and 0.005 eV/Å in force. A loose 12 × 12 × 1 Monkhorst–Pack $k$ grid is used during the optimization. To avoid any interaction between an MXene sheet and its periodically repeated images along the $c$ axis, a large vacuum space of 20 Å is used. After full structural optimization, a denser $k$ grid of 42 × 42 × 1 and 20 × 20 × 1 is employed in the calculation of electronic properties for PBE and HSE06, respectively. The computational cost of HSE06 precludes use of the largest $k$-point grids.

III. STRUCTURAL MODELS

In order to examine the evolution of the electronic properties of MXenes, we have studied the structural, magnetic, and electronic properties of a series of carbides Ti$_{n+1}$C$_n$ and nitrides Ti$_{n+1}$N$_n$, with $n$ up to 9. The 2D MXenes are constructed appropriately by removing “A” atoms from their bulk MAX phases (Fig. 1(b)). It is noteworthy that, for the parent MAX phases we used, the Ti$_2$AlC$_3$, Ti$_3$AlC$_2$, Ti$_4$GeC$_3$, (TiNb)$_5$AlC$_4$, Ti$_7$SnC$_6$, Ti$_2$AlN$_3$, and Ti$_4$AlN$_3$ have been synthesized experimentally. The unknown MAX phases
(Ti$_{n+1}$AlC$_n$, $n = 5, 7–9$, and Ti$_{n+1}$AlN$_n$, $n = 2, 4–9$) are built up by following a generalized modular building principle proposed by Etzkorn and co-workers.\textsuperscript{11} The calculated lattice parameters of all studied MAX phases are shown in Table I and compared with available experimental data\textsuperscript{14,34–38} and previous theoretical results\textsuperscript{25,39,40}. The consistency of the results in both experiment and theory make us confident for further studies. Notably, it has been reported that the surfaces of MXenes are covered with oxygen-containing groups, such as OH, and fluorine, F.\textsuperscript{16} As a consequence, the chemistry of exfoliated MXenes is expected to be closer to the functionalized MXenes than the bare material. It also could be possible to create O-termination surfaces by post-processing of OH-terminated systems.\textsuperscript{24}

### TABLE I. Calculated PBE equilibrium lattice parameter ($a$, $c$, and $c/a$) for MAX phases in comparison with available experimental data and previous theoretical results.

| Ti$_{n+1}$AC$_n$ | $a$ (Å) | $c$ (Å) | $c/a$ | Ti$_{n+1}$AN$_n$ | $a$ (Å) | $c$ (Å) | $c/a$ |
|-----------------|--------|--------|------|-----------------|--------|--------|------|
| Ti$_2$AlC       | PBE    | 3.0687 | 13.7266 | 4.47 | Ti$_3$AlN      | Theo\textsuperscript{a} | 3.0694 | 13.7311 | 4.47 |
| Theo\textsuperscript{a} | 3.065 | 13.71 | 4.48 | Exp\textsuperscript{b} | 2.9965 | 13.6400 | 4.55 |
| Exp\textsuperscript{b} | 2.986 | 13.60 | 4.55 |
| Ti$_3$AlC$_2$   | PBE    | 3.0816 | 18.6379 | 6.05 | Ti$_4$AlN$_2$  | PBE   | 3.0036 | 18.5007 | 6.16 |
| Theo\textsuperscript{a} | 3.0824 | 18.6522 | 6.05 | Theo\textsuperscript{a} | 3.0065 | 18.4780 | 6.15 |
| Exp\textsuperscript{b} | 3.075 | 18.58 | 6.04 |
| Ti$_4$GeC$_3$   | PBE    | 3.0868 | 22.8515 | 7.40 | Ti$_5$AlN$_3$  | PBE   | 2.9975 | 23.4828 | 7.83 |
| Theo\textsuperscript{d} | 3.088 | 22.852 | 7.40 | Theo\textsuperscript{d} | 2.9975 | 23.4828 | 7.83 |
| Exp\textsuperscript{e} | 3.088 | 22.852 | 7.40 | Exp\textsuperscript{e} | 2.9905 | 23.3800 | 7.82 |
| Ti$_5$AlC$_4$   | PBE    | 3.0791 | 28.7440 | 9.34 | Ti$_6$AlN$_4$  | PBE   | 2.9928 | 28.6249 | 9.56 |
| Theo\textsuperscript{g} | 3.074 | 28.76 | 9.35 | Theo\textsuperscript{g} | 3.00 | 28.44 | 9.48 |
| (TiNb)$_5$AlC$_4$ | Exp\textsuperscript{h} | 3.100 | 28.89 | 9.32 |
| Ti$_6$AlC$_5$   | PBE    | 3.0841 | 33.5105 | 10.86 | Ti$_7$AlN$_5$  | PBE   | 3.0011 | 33.3420 | 11.11 |
| Ti$_7$SnC$_6$   | PBE    | 3.1604 | 40.5154 | 12.82 | Ti$_8$AlN$_6$  | PBE   | 3.0017 | 38.2657 | 12.75 |
| Exp\textsuperscript{i} | 3.200 | 41.000 | 12.81 |
| Ti$_8$AlC$_7$   | PBE    | 3.0817 | 43.4258 | 14.09 | Ti$_9$AlN$_7$  | PBE   | 3.0036 | 43.1310 | 14.36 |
| Ti$_9$AlC$_8$   | PBE    | 3.0878 | 48.1608 | 15.59 | Ti$_{10}$AlN$_8$ | PBE | 3.0132 | 47.7686 | 15.85 |
| Ti$_{10}$AlC$_9$ | PBE    | 3.0885 | 53.1124 | 17.19 | Ti$_{11}$AlN$_9$ | PBE | 3.0145 | 52.6603 | 17.47 |

\textsuperscript{a} Ref. 25\textsuperscript{25} VASP–PBE.
\textsuperscript{b} Ref. 34\textsuperscript{34} XRD.
\textsuperscript{c} Ref. 14\textsuperscript{14} XRD.
\textsuperscript{d} Ref. 39\textsuperscript{39} DFT–GGA.
\textsuperscript{e} Ref. 35\textsuperscript{35} XRD.
\textsuperscript{f} Ref. 38\textsuperscript{38} XRD.
\textsuperscript{g} Ref. 36\textsuperscript{36} experiment, XRD/STEM; theory, CASTEP–GGA.
\textsuperscript{h} Ref. 40\textsuperscript{40} FPLAPW–GGA.
\textsuperscript{i} Ref. 37\textsuperscript{37} XRD/DSC/HRTEM.
Moreover, the hydrogen-terminated graphene has been studied extensively due to its unique properties\textsuperscript{11}. Therefore, in our studies, we have considered that the surfaces of MXenes are fully terminated by F, O, H, and OH, with a general formula of Ti\textsubscript{n+1}X\textsubscript{n}T\textsubscript{2} (X = C, N, and T is the terminations). Note, for MXenes extracted from the unknown MAX phases, only the fluorine termination has been studied. According to the geometry of the MXenes, the functionalized MXenes are built up with three major possible configurations: (I) all the functional groups are located above the hollow site of three neighboring C/N atoms and pointed to the Ti atoms in the second Ti atomic layer on both sides of MXenes; (II) all the functional groups are located on top the topmost sides of C/N atoms on both sides of MXenes; (III) is a combination of (I) and (II), in which one functional group is located on top of the hollow sites of C/N atoms on one side and another one locates above the top sites of C/N atoms on other sides. These models are shown in Fig. 2. We perform full geometry optimization for each of these structures.

IV. RESULTS AND DISCUSSION

A. Structural properties

We first check the relative stability of the different structural models. The PBE total energy differences (relative to configuration I) of all configurations and terminations are listed in Table II. Configuration I usually has the lowest total energy indicating it is energetically more favorable and the configuration III normally has the highest energy. This is quite understandable, since Ti atoms are the main electron donors and the functional groups are more likely to bond with Ti atoms than C or N atoms. However, there are several exceptions. For Ti\textsubscript{3}N\textsubscript{2}F\textsubscript{2}, configuration II has the lowest energy; whereas for Ti\textsubscript{4}N\textsubscript{3}(OH)\textsubscript{2} and Ti\textsubscript{7}C\textsubscript{6}H\textsubscript{2}, the configuration III is more stable. We also notice that the relative total energy differences are not very sensitive to increased layer thickness and oxygen always has the largest differences among the four functional groups for both carbides and nitrides. Moreover, the energy differences of nitrides are smaller than carbides. In general, our results are consistent with previous reports\textsuperscript{22,24}

We then proceed to investigate the ground-state structural properties of the functionalized MXenes. Some of the calculated equilibrium lattice parameters $a$, thickness of the
TABLE II. PBE total energy differences (relative to configuration I) of functionalized Ti$_{n+1}$C$_n$ and Ti$_{n+1}$C$_n$ MXenes. The most stable configuration is highlighted in bold-typeface.

| Ti$_{n+1}$C$_n$ | F  | O  | H  | OH | Ti$_{n+1}$N$_n$ | F  | O  | H  | OH |
|----------------|----|----|----|----|----------------|----|----|----|----|
|                | $E_0-E^I_0$ (eV) |       |       |       | $E_0-E^I_0$ (eV) |       |       |       |       |
| Ti$_2$C        | I  | 0.000 | 0.000 | 0.000 | 0.000 | I  | 0.000 | 0.000 | 0.000 | 0.000 |
|                | II | 0.439 | 1.750 | 0.698 | 0.321 | II | 0.398 | 1.175 | 0.533 | 0.296 |
|                | III| 0.215 | 0.769 | 0.365 | 0.130 | III| 0.427 | 0.546 | 0.299 | 0.266 |
| Ti$_3$C$_2$    | I  | 0.000 | 0.000 | 0.000 | 0.000 | I  | 0.000 |       |       |       |
|                | II | 0.729 | 1.423 | 0.718 | 0.476 | II | -0.089 |       |       |       |
|                | III| 0.371 | 0.712 | 0.349 | 0.240 | III| -0.002 |       |       |       |
| Ti$_4$C$_3$    | I  | 0.000 | 0.000 | 0.000 | 0.000 | I  | 0.000 | 0.000 | 0.000 | 0.000 |
|                | II | 0.720 | 1.462 | 0.719 | 0.455 | II | 0.161 | 1.102 | 0.591 | 0.003 |
|                | III| 0.387 | 0.733 | 0.361 | 0.245 | III| 0.088 | 0.561 | 0.299 | -0.003 |
| Ti$_5$C$_4$    | I  | 0.000 | 0.000 | 0.000 | 0.000 | I  | 0.000 |       |       |       |
|                | II | 0.701 | 1.491 | 0.720 | 0.429 | II | 0.051 |       |       |       |
|                | III| 0.362 | 0.747 | 0.358 | 0.222 | III| 0.057 |       |       |       |
| Ti$_6$C$_5$    | I  | 0.000 |       |       |       | I  | 0.000 |       |       |       |
|                | II | 0.720 |       |       |       | II | 0.146 |       |       |       |
|                | III| 0.369 |       |       |       | III| 0.08  |       |       |       |
| Ti$_7$C$_6$    | I  | 0.000 | 0.000 | 0.000 | 0.000 | I  | 0.000 |       |       |       |
|                | II | 0.712 | 1.532 | 0.205 | 0.419 | II | 0.093 |       |       |       |
|                | III| 0.361 | 0.780 | -0.154| 0.213 | III| 0.082 |       |       |       |
| Ti$_8$C$_7$    | I  | 0.000 |       |       |       | I  | 0.000 |       |       |       |
|                | II | 0.728 |       |       |       | II | 0.125 |       |       |       |
|                | III| 0.371 |       |       |       | III| 0.072 |       |       |       |
| Ti$_9$C$_8$    | I  | 0.000 |       |       |       | I  | 0.000 |       |       |       |
|                | II | 0.728 |       |       |       | II | 0.125 |       |       |       |
|                | III| 0.368 |       |       |       | III| 0.079 |       |       |       |
| Ti$_{10}$C$_9$ | I  | 0.000 |       |       |       | I  | 0.000 |       |       |       |
|                | II | 0.729 |       |       |       | II | 0.127 |       |       |       |
|                | III| 0.367 |       |       |       | III| 0.074 |       |       |       |
monolayer (vertical distance from the topmost atomic layer to bottommost atomic layer, $L$), and bond lengths between surface Ti atom and termination ($d_{\text{Ti-T}}$) and nearest C/N atom ($d_{\text{Ti-X}}$) with PBE and HSE06 functionals are shown and compared with other theoretical results in Table III. Clearly, our PBE results are in good agreement with others. The HSE06 lattice parameters and bond lengths are about 0.02 $\sim$ 0.03 Å smaller than for PBE.

| $\text{Ti}_{n+1}\text{C}_n\text{Ti}_2$ | $a$ (Å) | $L$ (Å) | $d_{\text{Ti-C}}$ (Å) | $d_{\text{Ti-T}}$ (Å) | $\text{Ti}_{n+1}\text{N}_n\text{Ti}_2$ | $a$ (Å) | $L$ (Å) | $d_{\text{Ti-N}}$ (Å) | $d_{\text{Ti-T}}$ (Å) |
|----------------------------------|---------|---------|----------------|----------------|----------------------------------|---------|---------|----------------|----------------|
| Theo.   | 3.0587  | 4.84    | 2.10          | 2.16          | Theo.   | 3.0704  | 4.69    | 2.07          | 2.16          |
| PBE     | 3.0583  | 4.80    | 2.10          | 2.16          | PBE     | 3.0642  | 4.63    | 2.07          | 2.16          |
| HSE     | 3.0312  | 4.72    | 2.08          | 2.14          | HSE     | 3.0460  | 4.55    | 2.05          | 2.14          |
| Theo.   | 3.0349  | 4.47    | 2.19          | 1.98          | Theo.   | 3.0191  | 4.28    | 2.17          | 1.93          |
| PBE     | 3.0329  | 4.45    | 2.19          | 1.98          | PBE     | 3.0030  | 4.35    | 2.15          | 1.98          |
| HSE     | 3.0093  | 4.40    | 2.17          | 1.96          | HSE     | 2.9743  | 4.29    | 2.13          | 1.86          |
| Theo.   | 3.0715  | 6.75    | 2.11          | 2.18          | Theo.   | 3.0635  | 6.68    | 2.08          | 2.17          |
| PBE     | 3.0712  | 6.79    | 2.12          | 2.18          | PBE     | 3.0635  | 6.66    | 2.08          | 2.17          |
| HSE     | 3.0464  | 6.71    | 2.09          | 2.17          | HSE     | 3.0447  | 6.56    | 2.06          | 2.16          |
| Theo.   | 3.0357  | 4.28    | 2.10          | 2.01          | Theo.   | 2.9882  | 4.20    | 2.07          | 2.00          |
| PBE     | 3.0394  | 4.24    | 2.08          | 1.99          | PBE     | 3.0127  | 4.11    | 2.04          | 2.00          |
| HSE     | 3.0093  | 4.40    | 2.17          | 1.96          | HSE     | 2.9743  | 4.29    | 2.13          | 1.86          |
| Theo.   | 3.0792  | 7.23    | 2.08          | 2.17          | Theo.   | 3.0704  | 4.69    | 2.07          | 2.16          |
| PBE     | 3.0775  | 7.21    | 2.08          | 2.17          | PBE     | 3.0226  | 7.15    | 2.07          | 2.15          |
| HSE     | 3.0508  | 7.14    | 2.06          | 2.15          | HSE     | 2.9945  | 7.07    | 2.04          | 2.14          |
| Theo.   | 3.0856  | 9.70    | 2.08          | 2.17          | Theo.   | 3.0827  | 9.45    | 2.06          | 2.15          |
| PBE     | 3.0844  | 9.67    | 2.07          | 2.17          | PBE     | 3.0268  | 9.62    | 2.06          | 2.15          |
| HSE     | 3.0582  | 9.58    | 2.05          | 2.16          | HSE     | 3.0041  | 9.49    | 2.04          | 2.14          |
| Theo.   | 3.0828  | 12.15   | 2.08          | 2.17          | Theo.   | 3.0704  | 12.09   | 2.07          | 2.15          |
| PBE     | 3.0794  | 12.19   | 2.08          | 2.17          | PBE     | 3.0226  | 12.09   | 2.07          | 2.15          |
| HSE     | 3.0528  | 12.09   | 2.06          | 2.15          | HSE     | 2.9947  | 11.96   | 2.04          | 2.13          |
| Theo.   | 3.0744  | 14.72   | 2.08          | 2.17          | Theo.   | 3.0235  | 14.52   | 2.05          | 2.16          |
| PBE     | 3.0456  | 14.63   | 2.06          | 2.15          | PBE     | 3.0235  | 14.52   | 2.05          | 2.16          |
| HSE     | 3.0456  | 14.63   | 2.06          | 2.15          | HSE     | 2.9932  | 14.37   | 2.04          | 2.13          |
| Theo.   | 3.0719  | 17.24   | 2.08          | 2.17          | Thi.    | 3.0222  | 16.97   | 2.05          | 2.15          |
| PBE     | 3.0441  | 17.13   | 2.06          | 2.15          | PBE     | 3.0222  | 16.97   | 2.05          | 2.15          |
| HSE     | 3.0441  | 17.13   | 2.06          | 2.15          | HSE     | 2.9945  | 16.78   | 2.03          | 2.14          |
| Theo.   | 3.0730  | 19.73   | 2.08          | 2.17          | Thi.    | 3.0194  | 19.45   | 2.05          | 2.15          |
| PBE     | 3.0442  | 19.61   | 2.08          | 2.15          | PBE     | 3.0194  | 19.45   | 2.05          | 2.15          |
| HSE     | 3.0442  | 19.61   | 2.08          | 2.15          | HSE     | 2.9913  | 19.23   | 2.03          | 2.13          |
| Theo.   | 3.0728  | 22.22   | 2.08          | 2.17          | Thi.    | 3.0200  | 21.87   | 2.05          | 2.15          |
| PBE     | 3.0453  | 22.08   | 2.06          | 2.15          | PBE     | 3.0200  | 21.87   | 2.05          | 2.15          |
| HSE     | 3.0453  | 22.08   | 2.06          | 2.15          | HSE     | 2.9932  | 21.62   | 2.03          | 2.13          |
| Theo.   | 3.0723  | 24.72   | 2.08          | 2.17          | Thi.    | 3.0179  | 24.34   | 2.05          | 2.15          |
| PBE     | 3.0448  | 24.56   | 2.06          | 2.15          | PBE     | 3.0179  | 24.34   | 2.05          | 2.15          |
| HSE     | 3.0448  | 24.56   | 2.06          | 2.15          | HSE     | 2.9874  | 24.13   | 2.03          | 2.13          |

$^a$ Ref. 24, VASP–PBE.
except for Ti$_2$NH$_2$, where the HSE06 lattice parameter is 0.15 Å longer. For both carbides and nitrides, the oxygen terminated MXenes have the shortest $d_{\text{Ti-T}}$ and longest $d_{\text{Ti-X}}$ bond length, implying a strong interaction between surface Ti atoms and O termination. Alternatively, the hydroxyl terminated MXenes have the largest lattice parameters and longest $d_{\text{Ti-T}}$ bond lengths. Comparing carbides with nitrides, we find that the carbides have larger lattice constant and longer bond lengths, correlating with the atomic radii difference between carbon and nitrogen. With increasing $n$, taking fluorinated MXenes as an example, the lattice constant of carbides increases initially, then decreases slowly when $n > 5$. On the other hand, the lattice constant of nitrides drops rapidly at $n = 2$, then it remains the same around 3.0 Å. For MXenes covered with other functional groups, similar behaviors have been observed.

**B. Magnetic and electronic properties**

We checked for possible magnetic ground states of MXenes with fully relaxed spin–polarized calculations. We find that only the Ti$_{n+1}$X$_n$ monolayers are magnetic. The magnetization results mainly from the 3$d$ electrons of surface Ti atoms. Taking Ti$_2$X as an example, the magnetic moments of surface Ti and topsite C/N atoms are about 0.982 and 0.065 $\mu_B$ per atom for Ti$_2$C and 0.619 and 0.027 $\mu_B$ per atom for Ti$_2$N, respectively.

![FIG. 3. (color online) Evolution of total magnetic moment of pure carbide (black line) and nitride (red line) monolayers as a function of the layer thickness. Carbides and nitrides behave differently.](image)
The total magnetic moment of carbides and nitrides as a function of $n$ are presented in Fig. 3. As we can see, carbides and nitrides show a different behavior. The total magnetic moment of carbides increases from 2 to 3 $\mu_B$, while in nitrides the total magnetic moment fluctuates around 1.2 $\mu_B$. Upon functionalization, the magnetism of MXenes disappeared.

With the appropriate ground-states, we can now move to study the electronic properties of functionalized MXenes. We first examine the electronic properties of the thinnest Ti$_2$XT$_2$ monolayers. The calculated PBE and HSE06 band structures of Ti$_2$XT$_2$ monolayers are shown and compared with pure MXenes and parent MAX phases in Fig. 4. The PBE and HSE06 functionals give the similar results, and all of these materials are metals, with the notable exception of Ti$_2$CO$_2$. PBE functional predicts a band gap of 0.24 eV for Ti$_2$CO$_2$, while the gap is widened to 0.88 eV by HSE06 hybrid functional. Since HSE06 is expected to be more reliable than PBE for band gaps, we predict a near 1eV band gap for this material. Unless specifically mentioned, the following results are all calculated with HSE06.

By examining the band structures near the Fermi level, we find that the Fermi energy
FIG. 5. (color online) (a) and (b) Partial density of states of Ti$_2$CT$_2$ and Ti$_2$NT$_2$, and related MXenes and MAX phase computed using the HSE06 functional.

shifts down after removing Al atoms from MAX phases, and then it shifts down in energy again after the MXenes surfaces are terminated (Fig. 4). To give a better description of the electronic properties, the partial density of states (PDOS) of these materials are shown in Fig. 5. As we can see, for MAX phases, the DOS at Fermi level ($N(E_F)$) is dominated by Ti 3$d$ orbitals. The valence states below Fermi level can be divided into two sub-bands which are formed by hybridized Ti 3$d$–C 2$p$ and Ti 3$d$–Al 3$s$ orbitals between -10 and -3 eV (band B), and Ti 3$d$–Al 3$p$ orbitals near Fermi level (band A). These mixed states correspond to the Ti–C and Ti–Al bands. By extracting Al atoms, the bands A and B are narrowed, and a gap opens between them. The $N(E_F)$ increases from 1.88 to 3.15 and from 2.77 to 4.84 for carbides and nitrides, due to the breaking of Ti–Al bonds, respectively. After functionalization, the Fermi level shifts to lower energy states and the $N(E_F)$ decreases due to the new energy states between Ti and terminations. For carbides, band C is formed below band B corresponding to the hybridization between Ti and functional groups. Different from carbides, except for the newly formed band C, the functional groups also have a large contribution for band B in nitrides. Comparing Ti$_2$CO$_2$ with other materials, we find that
TABLE IV. Evolution of DOS at Fermi level as a function of \( n \) of functionalized MXenes computed using the HSE06 functional.

| Ti\(_{n+1}\)C\(_n\) | O  | F  | H  | OH | Ti\(_{n+1}\)N | O  | F  | H  | OH |
|-------------------|----|----|----|----|-------------|----|----|----|----|
| Ti\(_2\)C         | 0  | 2.156 | 0.566 | 1.916 | Ti\(_3\)N   | 2.562 | 0.941 | 1.045 | 1.817 |
| Ti\(_3\)C\(_2\)    | 0.575 | 2.026 | 0.823 | 2.876 | Ti\(_4\)N\(_2\) | 3.895 | 2.601 | 2.313 | 3.881 |
| Ti\(_4\)C\(_3\)    | 0.98 | 2.013 | 2.902 | 3.176 | Ti\(_5\)N\(_3\) | 4.013 | 4.895 |
| Ti\(_5\)C\(_4\)    | 0.915 | 4.392 | 5.124 | 4.013 | Ti\(_6\)N\(_4\) | 3.407 |
| Ti\(_6\)C\(_5\)    | 7.284 | Ti\(_7\)N\(_5\) | 6.501 |
| Ti\(_7\)C\(_6\)    | 0.998 | 6.579 | 8.082 | 6.214 | Ti\(_8\)N\(_6\) | 4.072 |
| Ti\(_8\)C\(_7\)    | 5.835 | Ti\(_9\)N\(_7\) | 7.363 |
| Ti\(_9\)C\(_8\)    | 5.444 | Ti\(_10\)N\(_8\) | 8.107 |
| Ti\(_10\)C\(_9\)   | 5.248 | |

band B is equally contributed by Ti 3\(d\), C 2\(p\), and O 2\(p\) orbitals. The strong hybridization of Ti 3\(d\)–C 2\(p\) and Ti 3\(d\)–O 2\(p\) is responsible for the semiconducting behavior of Ti\(_2\)CO\(_2\).

Since the \( N(E_F) \) is very important for the surface chemistry of layered materials, the evolution of the value of \( N(E_F) \) of functionalized MXenes as a function of \( n \) has been studied and is shown in Table IV. Firstly, we notice that starting from \( n = 2 \), the carbides with oxygen termination are metals. By looking at the PDOS Ti\(_{n+1}\)C\(_n\)O\(_2\) (Fig. 6), it is clear that the contribution of O 2\(p\) orbitals to band B decreases as \( n \) increased. Starting from \( n = 2 \), Band B is dominated by mixed Ti 3\(d\) and C 2\(p\) bands and connected with band A, which is similar to the case observed in MAX phases. Therefore, the weaker Ti–O coupling in energy states B results in the metallic phase of Ti\(_{n+1}\)C\(_n\)O\(_2\). Secondly, we find that, for carbides, the fluorine terminated MXenes have the largest DOS at Fermi level and the oxygen terminations have the lowest one, while it is opposite for nitrides. Thirdly, there is a clear trend that, for both carbides and nitrides covered with functional groups, the value of \( N(E_F) \) increases with increased \( n \). For instance, taking fluorinated MXenes as an example, \( N(E_F) \) of Ti\(_{n+1}\)C\(_n\)F\(_2\) is around 2 for \( n \leq 3 \), then it increases rapidly from 2.013 \( (n = 3) \) to 7.284 \( (n = 5) \), which is about 3.5 times higher. It decreases slowly to 5.248 \( (n = 9) \), which is still 2.5 times higher than the thinnest MXenes. Alternatively, \( N(E_F) \) of Ti\(_{n+1}\)N\(_n\)F\(_2\) continuously increases from 0.941 \( (n = 1) \) to 8.107 \( (n = 9) \), which is about 8 times higher. The similar behavior is also observed in MXenes with other functional groups. The huge difference of \( N(E_F) \) between the thin \( (n < 5) \) and thick \( (n \geq 5) \) functionalized MXenes implies their surface properties should be very different and the thick layers may
FIG. 6. (color online) Partial density of states of Ti$_{n+1}$C$_n$O$_2$ up to $n = 4$ computed using the HSE06 functional.

have higher chemical activity. The conductivity is expected to be similarly effected.

To better understand the trend, we examine the PDOS of Ti$_{n+1}$X$_n$F$_2$ as a function of $n$ as shown in Fig. 5 and compare it with bulk titanium carbide (TiC) and nitride (TiN). One can observe that at $n = 1$, the peak of the conduction states is about 2 eV above the Fermi level for both carbide and nitride. This can also be seen from the band structures (Fig. 8). We also find that, for carbide, there are energy bands crossing the Fermi level along all the high symmetry directions of the Brillouin Zone. However, the energy bands only cross the Γ–M and K–Γ directions in nitride. This could be the reason that $N(E_F)$ of Ti$_2$NF$_2$ is about half of Ti$_2$CF$_2$. With increasing $n$, the Fermi level shifts down continuously and there are more bands forming near the Fermi level (Fig. 8) related to the Ti–C coupling (Fig. 7).

For carbides, we observe a sharp narrow DOS peak appears around 0.5 eV above the Fermi level at $n = 3$, corresponding to the less dispersed band along the Γ–M–K direction (Fig. 8(a)). This peak shifts down and come across the Fermi level at $n = 4$, where we start to see the increasing of $N(E_F)$. The latter reaches the maximum when Fermi level locates at the top of this peak at $n = 5$. For higher $n$, this band keeps shifting down and goes below
FIG. 7. (color online) (a) and (b) Partial density of states of Ti$_{n+1}$C$_n$F$_2$ and Ti$_{n+1}$N$_n$F$_2$, compared with bulk TiC and TiN phase, computed using the HSE06 functional.

FIG. 8. (color online) (a) and (b) Band structures of Ti$_{n+1}$C$_n$F$_2$ and Ti$_{n+1}$N$_n$F$_2$ at $n = 1, 3, 5, 7,$ and $9$ computed using the HSE06 functional. Clearly, there are more bands forming near the Fermi level with increased $n$. 
the Fermi level (Fig. 8(a)). Moreover, there are fewer bands cross the Fermi level in the K–Γ direction. Although a new band is approaching the Fermi level, the value of $N(E_F)$ is still decreased. For nitrides, we don’t see the sharp narrow DOS peak as well as the flat band above the Fermi level as in carbides. Due to the shifting down of the Fermi level, the bands start to cross the M–K direction at $n = 2$, and steadily increasing numbers of bands cross the Γ–M and K–Γ directions as $n$ increases. Therefore, we observe a continuous increasing of $N(E_F)$ in nitrides. We should point out, for $n = 5$, and 7, the Fermi level is located in the bottom of a small valley, so the $N(E_F)$ decreases a little compared to other nitrides. Moreover, the DOS of carbides and nitrides show some characters as of bulk TiC and TiN when $n \geq 7$. However, the contribution of C 2$p$ orbital near the Fermi level is more significant in the thicker MXenes than bulk. Thus, the thicker MXenes can still be considered as 2D materials.

V. CONCLUSION

In summary, we have systematically studied the structural and electronic properties of functionalized Ti$_{n+1}$C$_n$ and Ti$_{n+1}$N$_n$ with $n$ up to 9, using PBE and HSE06 functionals. We show that both PBE and HSE06 predict very similar structures and electronic structures. The HSE06 functional predicts structural parameters smaller than PBE by $0.02 \sim 0.03$ Å and gives similar band structures. The functional groups are more likely to bond with Ti atoms as the electron donor. Without terminations, MXenes are magnetic, with the magnetism primarily due to surface Ti atoms. Upon functionalization, the magnetism is removed. All the functionalized MXenes are metallic except for semiconducting Ti$_2$CO$_2$, due to the strong Ti 3$d$ and O 2$p$ orbital hybridization near the Fermi level. The electronic properties of thicker MXenes ($n \geq 5$) are different from the thinnest, where the $N(E_F)$ of thicker MXenes is about $3.5 \sim 8$ times higher. This indicates that the thinnest and more thick MXenes are likely to display differing properties. Our simulations shed some light on selecting proper MXene systems for possible applications and future experimental and theoretical studies are encouraged in this field.
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