Electronic Nature Transition and Magnetism Creation in Vacancy-Defected Ti$_2$CO$_2$ MXene under Biaxial Strain: A DFTB + U Study

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ABSTRACT: The structural, electronic, and magnetic properties of vacancy defect in Ti$_2$CO$_2$ MXene and the effect of strain have been investigated using the density functional tight-binding (DFTB) approach including spin-polarization with Hubbard onsite correction (DFTB + U). The band gap of pure Ti$_2$CO$_2$ is $\sim$1.3 eV, which decreases to $\sim$0.4 and $\sim$1.1 eV in the case of C- and O-vacancies, respectively, i.e., the semiconducting behavior is retained. In contrast, Ti$_2$CO$_2$ undergoes semiconductor-to-metal transition by the introduction of a single Ti-vacancy. This transition is the result of introduced localized states in the vicinity of the Fermi level by the vacancy. Both Ti- and O-vacancies have zero net magnetic moments. Interestingly, the nonmagnetic (NM) ground state of semiconducting Ti$_2$CO$_2$ turns into a magnetic semiconductor by introducing a C-vacancy with a magnetization of $\sim$2 $\mu_B$/cell. Furthermore, we studied the effect of strain on the electronic structure and magnetic properties of Ti$_2$CO$_2$. The nature of the band gap in the presence of single O-vacancy remains indirect in both compression and tensile strain, and the size of the band gap decreases. Compression strain on Ti-vacant Ti$_2$CO$_2$ changes metal into a direct semiconductor, and the metallic character remains under tensile biaxial strain. In opposition, a semiconductor-to-metal transition occurs by applying a compressive biaxial strain on C-vacant Ti$_2$CO$_2$. We also find that the magnetism is preserved under tensile strain and suppressed under compression strain on V$_x$Ti$_2$CO$_2$. Moreover, we show that double C-vacancies maintain magnetism. Our findings provide important characteristics for the application of the most frequent MXene material and should motivate further investigations because experimentally achieved MXenes always contain point defects.

INTRODUCTION

In recent years, intensive efforts have been paid to the development of novel two-dimensional (2D) materials, such as the MXene material family due to their similar structure to graphene. However, compared to graphene, some MXenes have excellent properties such as a medium band gap, high thermal stability, and high conductivity and carrier mobility, which allow them to be applied in a broad range of applications, i.e., energy materials, nanoelectronics, catalysts, chemical sensors, etc.

Briefly, MXenes are constituted by intercalated atomic layers of transition metal atoms and of carbon following the general formula $\text{M}_{n+1}\text{X}_n\text{T}_p$, where M is a transition metal, X is carbon/nitrogen, and T stands for a terminated group (O, OH, F). Generally, MXenes are obtained by etching off the A element from their host, layered ternary MAX phases, resulting in a formula of $\text{M}_{n+1}\text{X}_n\text{T}_p$. Carbide MXenes show high conductivity, high oxidation resistance, and easily tunable surface terminations, which make them potential candidates for energy storage applications, supercapacitors, sensors, carbon capture technologies, and heterogeneous catalysts. Studies on MXenes suggest that most titanium-based MXenes without surface functionalization show metallic behavior, and the electronic properties could be modulated by surface terminations. However, Ti$_2$CO$_2$ shows semiconductor characteristics with an indirect band gap.

Surface termination is an appropriate way to modulate the electronic structure. Various experimental techniques for characterizing the surface functional groups such as simple oxidation have already been confirmed by X-ray photoelectron spectroscopy (XPS) analysis, nuclear magnetic resonance (NMR) spectroscopy, neutron diffraction, and scanning transmission electron microscopy-electron energy loss spectroscopy (STEM-EELS). Moreover, Ibragimova et al. confirmed that the distribution of the T functional group (T = O, OH, and F) on the Ti-based MXene surface is related to experimental parameters such as the etching solution pH value, etching temperature, and work function. Ti$_2$CT$_x$ MXene has been successfully fabricated from its parental Ti$_3$AlC$_2$ phase in 2012. From a theoretical point of view, density functional theory
(DFT) calculations have been used to investigate the electronic structures of Ti_{x}CO_{2} terminated with F, O, and OH, respectively. Ti_{x}CO_{2} was predicted to be a semiconductor with an indirect band gap,\(^{25,27-29}\) high carrier mobility,\(^{25,26,37}\) high thermodynamic stability,\(^{38}\) and strong excitonic effect.\(^{27,39}\) Moreover, the pure carbide MXene monolayers are magnetic, while functionalization removes magnetism.\(^{40}\) In addition, surface functionalization is also a critical factor that modifies the fundamental properties of MXenes.\(^{41,42}\) First-principles calculations of V_{2}C showed a metallic character of bare V_{2}C, which is preserved for all surface groups.\(^{43}\) The magnetic ground state of Mn_{2}C can be switched from antiferromagnetic (AFM) to ferromagnetic (FM) by full hydrogenation/oxygenation.\(^{44}\) The surface termination of Ti_{x}N_{y} with a −OH group modifies it from FM metal to NM.\(^{45}\) From the theoretical point of view, Ti_{2}C can exhibit different electronic and magnetic behaviors. Ti_{2}C was shown to be a typical semiconductor system with an electronic band gap of about 0.2 eV.\(^{46}\) The A-AFM configuration was favored over FM, C-AFM, and G-AFM in a Ti_{2}C system,\(^{47}\) where A-AFM means a ferromagnetic alignment between intralayer Tis and antiferromagnetic ordering among the top and bottom layers, while in the C-type (G-type) structure, spins are arranged antiferromagnetically within each Ti layer and ferromagnetically (antiferromagnetically) ordered between lines of the top and bottom layers.\(^{48-50}\) Recently, Ketolainen et al. showed that the ground state of Ti_{2}C is an AFM semiconductor.\(^{51}\) The electronic band gap was calculated to be 0.18 and 0.32 eV using the Perdew–Burke–Ernzerhof (PBE) and the Heyd–Scuseria–Ernzerhof (HSE06) hybrid functional, respectively. However, the magnetic ground states can also have FM alignment. Gao et al. showed that Ti_{2}C exhibits nearly half-metallic behavior and that the FM state is more energetically stable than the AFM and NM ones.\(^{52}\) It was also revealed that a pristine Ti_{2}C monolayer acts as a metal.\(^{26,53}\) Moreover, when two surfaces are saturated by an oxygen atom, the newly formed material (Ti_{x}CO_{2}) presents a semiconducting behavior (the band gap of 1.32 eV from the accurate many-body GW method)\(^{50}\) with a superhigh carrier mobility\(^{25,26}\) and high thermodynamic stability.\(^{38}\) The excellent properties of Ti_{x}CO_{2} ensure its use in potential applications, such as gas sensors,\(^{54}\) optical devices,\(^{27,51}\) thermoelectric materials,\(^{52}\) catalysts,\(^{53,54}\) and anchoring materials for lithium–sulfur (Li–S) batteries.\(^{55,56}\) Ti_{x}CO_{2} MXene was synthesized\(^{35}\) and has been demonstrated to show many interesting properties.

On the other hand, lattice imperfections could be present in 2D materials. It may deteriorate the performance of materials. However, the conductance and electronic properties could be governed by defects. Defect engineering is essential for tailoring properties and achieving new functionalities in materials science,\(^{57-59}\) and it has been proven to be an effective way to introduce interesting properties.\(^{60-62}\) Moreover, realistic MXene structures always contain defects like a titanium vacancy,\(^{1,3,36,63,64}\) carbon vacancy,\(^{1,3,36,63,64}\) and oxygen vacancy.\(^{1,3,36,63,64}\) It is evident that the defects and strain play a crucial role in tailoring the properties of 2D materials. Strain can be generated by epitaxy or by external loading on small-volume or bulk-scale nanomaterials.\(^{69}\) Previous research studies stipulate that strain is a way to modulate the electronic properties of materials.\(^{70,71}\) By applying a strain, the properties of the materials are affected because of the changes in the distance and the relative position of atoms,\(^{72-74}\) and thus, the electronic structure is significantly adjusted.\(^{75}\) The band gap of Ti_{x}CO_{2} can be modulated from indirect type to direct type by strain.\(^{51}\) Here, the influence of vacancy defects and strain on the electronic and magnetic properties of Ti_{x}CO_{2} MXene is systematically studied by means of the DFTB + U method.

### COMPUTATIONAL DETAILS

DFTB is an elegant formalism that allows for a detailed electronic description while minimizing the degree of empiricism, as the key parameters can be directly derived from traditional DFT. In this paper, the spin-polarized self-consistent-charge density functional tight-binding (SCC-DFTB) approach was employed from the DFTB+ package\(^{76,77}\) in conjunction with mio\(^{53}\) and its extensions trans3d\(^{79}\) Slater–Koster parameter set available at https://dftb.org/. In this method, a tight-binding approximation is applied to the DFT Kohn–Sham Hamiltonian, and the matrix elements of the simplified Hamiltonian are determined by self-consistent redistribution of Mulliken charges. SCC-DFTB enables treatments for much bigger systems quite efficiently yet with reasonably high accuracy. The DFTB method has been extensively used in the modeling of carbon-based materials.\(^{80-83}\) In this work, we considered the U correction for 3d shells of the titanium atoms. The U was set to 3 eV based on reported values in the
literature.\textsuperscript{84,85} Using the Hubbard U model can significantly improve the value of the electronic band gap and the magnetism in the system. The vacancy-defected Ti$_2$CO$_2$ is modeled by a 5 × 5 × 1 supercell (50 Ti, 25 C, and 50 O atoms). The SCC convergence threshold is defined by the maximum change between two succeeding SCC cycles. In the calculation, self-consistent charges have been set to a relative difference of 10\%.

Our results have been compared with a mixing parameter of 0.2. The geometry was initially relaxed such that all forces were less than 10^{-4} \text{ au}, which provided the initial geometry for equilibration. Biaxial strains were realized by stretching or compressing the 5 × 5 × 1 supercells in the xy plane by ±0, ±2, ±3, ±4, ±5, ±6, and ±7\%. Strains can be introduced easily and do not produce obvious structural phase transitions. All atomic structures were visualized by VESTA.\textsuperscript{57} We also performed molecular dynamics (MD) simulation, the computational details of which are given in the Supporting Information.

## RESULTS AND DISCUSSIONS

### Pure Ti$_2$CO$_2$ MXene

Ti$_2$C MXene crystallizes in the P\textoverline{3}m1 space group (No. 164), and it consists of three atomic sheets with a hexagonal-like unit cell, where one C atomic layer is sandwiched by two Ti layers. Ti and C atoms occupy 4f (1/3, 2/3, z$_\text{Ti}$) and 2a (0, 0, 0) Wyckoff positions, respectively. The most energetically favorable termination sites for the O atom are at the hollow sites between three neighboring carbon atoms on both sides of the Ti$_2$C sheets, corresponding to the configuration [O/Ti$_2$C/O]$_\text{13,51,88,89}$. It has already been confirmed that this model is the most stable structure of titanium-based MXenes functionalized with oxygen\textsuperscript{51} among other models. Here, a fully O-terminated Ti$_2$C monolayer is chosen and O adsorbed on 2c (0, 0, z$_\text{O}$). The crystal structure of the Ti$_2$CO$_2$ supercell is shown in Figure 1.

As a preliminary test, we start by calculating the structural parameters of the pristine Ti$_2$CO$_2$ system, which can be viewed as a benchmark calculation. The DFTB-optimized lattice constant, bond length, and electronic band gap of the Ti$_2$CO$_2$ monolayer are listed in Table 1. Our results have been compared to previously published PBE, HSE06, and GW results. Overall, our data on lattice parameters and bond lengths of the present system are in good agreement with the former calculation results, suggesting the reliability of the computations in the present study.

We evaluate the stability of Ti$_2$CO$_2$ by calculating the cohesive energy, defined as $E_{\text{coh}}=(-E_{\text{Ti}_2\text{CO}_2} + 2 \times E_{\text{Ti}} + E_{\text{C}} + 2 \times E_{\text{O}})/5$, where $E_{\text{Ti}}$, $E_{\text{C}}$, and $E_{\text{O}}$ are the total energies of free Ti, free C, and free O atoms, respectively. $E_{\text{Ti}_2\text{CO}_2}$ denotes the total energy of one unit cell of Ti$_2$CO$_2$. S refers to the number of atoms in the Ti$_2$CO$_2$ monolayer. We find a value of 10.96 eV/atom, which is in accordance with the PBE result found in the literature; i.e., 7.10\% and 9.78 eV/atom.\textsuperscript{90}

Using the DFTB method, we found a band-gap value of Ti$_2$CO$_2$ of 0.71 eV, which is higher than the previous PBE value (between 0.24 and 0.35 eV)\textsuperscript{1,36} and a bit lower than the HSE06 functional.\textsuperscript{6,13,36} An agreement between the lattice parameter, Ti–O and Ti–C distances, and the electronic band gap from DFTB and DFT methods can be seen in Table 1, indicating that the DFTB method works quite well for the system we are interested in. Moreover, it was reported that the PBE functional largely underestimates the band-gap size of the semiconductors, while HSE06 and GW can serve to obtain a more accurate energy gap of 2D semiconductors.\textsuperscript{93,94} In Figure 2, we plot the electronic band structure of the Ti$_2$CO$_2$ monolayer calculated by DFTB + U. We found that the Ti$_2$CO$_2$ monolayer shows a Γ (valence band maximum) to M (conduction band minimum) indirect band gap. In our DFTB + U calculations (U = 3 eV), we achieved an accurate band gap of Ti$_2$CO$_2$ of about 1.29 eV. This value is close to the GW results of Zhang et al. (1.15 eV)\textsuperscript{6} and Ding et al. (1.32 eV).\textsuperscript{39} It was confirmed that GW is known to provide an accurate description of the electronic structures of 2D materials,\textsuperscript{45} therefore, the rest of the study will be conducted using the DFTB + U method.

### Vacuum Defect in Ti$_2$CO$_2$

**Single Ti, C, and O-Vacancies in Ti$_2$CO$_2$**

Vacancy defects are unavoidable during the preparation of the MXene materials, and thus, the properties of Ti$_2$CO$_2$ can be affected by introducing defects. The Ti-vacancy was detected during the preparation of MXene;\textsuperscript{63} the C-vacancy intrinsically exists in MAX phase materials;\textsuperscript{96} and the O-vacancy has been investigated.\textsuperscript{97} Here, we considered three types of single atom vacancy (V$_{\text{Ti}}$, V$_{\text{C}}$, and V$_{\text{O}}$) in Ti$_2$CO$_2$ MXene. Titanium, carbon, and oxygen deficiency models are constructed by removing one Ti, C, or O atom from a 5 × 5 × 1 Ti$_2$CO$_2$ supercell, which corresponds to a concentration of

| DFTB | PBE | HSE06 | GW |
|------|-----|-------|----|
| $a=b$ (Å) | 3.01 | 3.01\textsuperscript{13,36,40} | 3.01\textsuperscript{89} | 3.01\textsuperscript{91} |
| Ti–C (Å) | 2.15 | 2.17\textsuperscript{13,36,39} | 2.18\textsuperscript{40} | 2.19\textsuperscript{92} |
| Ti–O (Å) | 2.00 | 1.96\textsuperscript{13,36,39} | 1.97\textsuperscript{40} | 1.98\textsuperscript{92} |
| $E_{\text{coh}}$ (eV) | 0.71 | 0.24–0.35\textsuperscript{13,36,40} | 0.85–0.92\textsuperscript{41,36,40,42,75} | 1.15\textsuperscript{6} | 1.32\textsuperscript{39} |
| E$_{\text{Fermi}}$ (eV) | 1.29 (DFTB + U) | 0.67 (PBE + U) | | |

Figure 2. (Color online) Electronic band structure of the Ti$_2$CO$_2$ monolayer computed with DFTB + U. The Fermi level ($E_{\text{Fermi}}$) is set to zero.
The three systems with Ti-, C-, and O-vacancies are named $V_{\text{Ti}}\text{-Ti}_2\text{CO}_2$, $V_{\text{C}}\text{-Ti}_2\text{CO}_2$, and $V_{\text{O}}\text{-Ti}_2\text{CO}_2$, respectively, and they are presented in Figure 3. The lattice parameter is 3.01 Å. Therefore, the distance between neighbor vacancies is 15.05 Å, so that the vacancies are isolated.

The calculated structural parameters of $V_{\text{Ti}}\text{-Ti}_2\text{CO}_2$, $V_{\text{C}}\text{-Ti}_2\text{CO}_2$, and $V_{\text{O}}\text{-Ti}_2\text{CO}_2$ systems change slightly when compared with that of the pristine Ti$_2$CO$_2$ monolayer. Bond lengths close to the created vacancy, the vacancy formation energy, and the electronic band gap values are given in Table 2.

To assess the formation tendency of different vacancies, the vacancy formation energies $E_f$ for Ti-, C-, or O-vacancy defects are calculated using the following equation:

$$E_f = -E_{\text{pristine}} + E_{\text{vac}} + E_{\text{atm}}$$

where $E_{\text{pristine}}$ is the total energy of pure Ti$_2$CO$_2$, $E_{\text{vac}}$ denotes the total energy of a Ti$_2$CO$_2$
monolayer with a single vacancy, and $E_{\text{tot}}$ refers to the total energy per atom forming the defect (Ti, C, or O atom).

We found that the C-vacancy exhibits the lowest formation energy when compared to that of Ti- and O-vacancies, indicating that carbon vacancy is most likely to be formed in Ti$_2$CO$_2$ in accordance with the ref 2. Moreover, the Ti-vacancy is the most energetically demanding than C-vacancy and O-vacancy, which is consistent with the conclusion of previous research studies.\(^2,6^4\) Ti-vacancy creation is not easy to occur when compared with other types of vacancies, but it can be induced in nonequilibrium processes such as e-beam lithography,\(^9^9\) which was used to decorate the vacancy defects in the MoS$_2$ monolayer.\(^9^9\)

The creation of a C-vacancy makes the Ti atoms near the C-vacancy away from the vacancy by the remaining strengthened p$-d$ bonds of V$_C$-Ti$_2$CO$_2$. The creation of a Ti-vacancy makes the formation of unsaturated electrons on the nearest C/O atoms, which results in stronger interactions between C/O atoms and their nearest Ti atoms. The creation of an O-vacancy on the surface of the Ti$_2$CO$_2$ monolayer makes the charge redistribution and results in the formation of the stronger Ti$-O$ and Ti$-C$ bonds near the O-vacancy. It is worth noting that the vacancy formation energies calculated by DFT + U are consistent with the ones calculated by DFT, which proves the accuracy of the used method.

In Figure 4, we plot the band structures of single Ti-, C-, and O-vacancy defects in Ti$_2$CO$_2$ MXene. We clearly remark a semiconductor-to-(semi)metal transition after Ti-vacancy creation. The localized states in the vicinity of the Fermi level introduced by the Ti-vacancy tend to introduce a metallic behavior in Ti-vacant Ti$_2$CO$_2$. Moreover, we can see that there is an increased electronic density at the Fermi level, which indicates the improvement of the electrical conductivity of Ti$_2$CO$_2$. Results are consistent with available DFT studies.\(^3,6^6\) However, Wang et al. found a PBE-DFT band gap energy of 0.33 for pure Ti$_2$CO$_2$, which is calculated to be 0.05 eV in the presence of the Ti-vacancy.\(^1\) On the other hand, the inclusion of the U term (PBE + U) predicted a 0.67 eV gap of the pure material and a 0.0 eV gap (semimetal) in V$_T$-Ti$_2$CO$_2$.\(^3\) We will discuss more in the section on strain below. By C- and O-vacancy creation, Ti$_2$CO$_2$ maintains its semiconducting characteristics, which is in line with DFT calculations.\(^6^5,1^0^0\)

The electronic band structure analysis reveals that the band gaps in C- and O-vacancy systems changed from a wide band gap of 1.29 eV (pristine Ti$_2$CO$_2$) to lower band gaps of 0.36 and 1.12 eV, respectively. Using DFT for a 3 $\times$ 3 $\times$ 1 Ti$_2$CO$_2$ supercell, Xiao-Hong et al.\(^6^4\) found that the introduction of C- and O-vacancy defects result in a transition from semiconductor to metal. From their calculated partial density of states, the Fermi level in V$_C$ and V$_O$-Ti$_2$CO$_2$ is very close to the edge of the conduction band. The Hubbard U parameter is very important in this case. Adding the U parameter can increase the conduction band minimum level, and the gap may be opened.

On the other hand, most available studies on defected Ti$_2$CO$_2$ do not consider spin-polarization.\(^3,3^6,4^2,6^6,7^0\) In the present spin-polarized calculations, we found that Ti$_2$CO$_2$ is NM even after introducing Ti$-O$ vacancy, in accordance with refs 3, 65. Moreover, DFTB + U calculations reveal that C-vacancy creation tunes the magnetism; we obtained a total magnetic moment of 1.95 $\mu_B$ for the structure. We note that using PBE calculations, Bandypadhyay et al.\(^1^2\) claimed that C-vacant Ti$_2$CO$_2$ is nonmagnetic. To be sure that obtained magnetism is not an artifact of our DFTB + U method, we performed additional PBE-DFT calculations (see Supporting Information, Table S1 and Figure S1). We show that there is no magnetism without the U parameter. If we enforced a fixed magnetic moment of 2 $\mu_B$ per cell, the PBE-DFT ferromagnetic solution was 0.06 eV above. However, by applying an increasing value of the U parameter to the Ti atom, we found a natural magnetic behavior for V$_C$ in a 3 $\times$ 3 $\times$ 1 Ti$_2$CO$_2$ supercell with a total magnetic moment of 2 $\mu_B$ (see Table S1). Further, we calculated the electronic structure of 3 $\times$ 3 $\times$ 1 V$_O$-Ti$_2$CO$_2$ by hybrid HSE06 DFT to double-check if we obtained the right physics. Again, we obtained a ferromagnetic behavior with a total magnetic moment of 2 $\mu_B$ per cell (the nonmagnetic solution was 0.05 eV above). Finally, we performed DFT + U (U = 3 eV)

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure5.png}
\caption{(Color online) Electronic band gap (top) and strain energy (bottom) of single Ti-, C-, and O-vacancies on the 5 $\times$ 5 $\times$ 1-Ti$_2$CO$_2$ supercell under biaxial strain. Dashed lines are a guide to the eye.}
\end{figure}
calculations on a $5 \times 5 \times 1$ supercell with $V_C$ as obtained from DFTB + U and confirmed the magnetism (see Figure S1 for spin density distribution; the nonmagnetic solution was 0.07 eV above).

**Strain Effects on $V_{Ti}$, $V_C$, and $V_{O-Ti_2CO_2}$.** It was shown that mechanical strain is a prominent approach to modulating electronic properties.$^{51,101}$ In the present work, the strain is calculated as $\varepsilon = \frac{(a - a_0)}{a_0} \times 100$, where $a_0$ and $a$ are the lattice constants of the cell without and with strain, respectively. Biaxial strain from $-7$ to $+7\%$ is applied to study the band gap variation of $V_{Ti}$, $V_C$, and $V_O$ in a $5 \times 5 \times 1$-Ti$_2$CO$_2$ supercell (vacancy concentration of 0.8%). Here, negative and positive values of $\varepsilon$ indicate the strain state and the model under a tensile strain, respectively. Compressive and tensile strain is assumed by setting the calculated lattice parameter to a fixed smaller/larger value and relaxing the atomic positions. The strain modifies the bond length and changes the coupling between the atoms, and therefore it manipulates the electronic structure.

The elastic limit of the strain was checked by calculating the strain energy per atom, defined as $E_{\text{strain}} = \frac{E_{\text{max}} - E_{\text{min}}}{n}$, where $n$ is the number of atoms in the supercell. By definition, the strain energy represents the energy obtained from deforming supercell and its ability go back to its original shape as soon as possible. In Figure S5, we plot the variation of the strain energy as a function of the strain. The strain energy curve shows a quadratic function, which indicates that all strains present an elastic range and they are fully reversible. The stability of the Ti-, C-, and O-vacancies under a $\pm 7\%$ strain have been explored by performing the constant temperature molecular dynamics simulations, and we found that these defects are quite stable at room temperature under strain (see the Supporting Information for details: Figures S10 and S11 and Table S2).

Variations of the electronic band gaps of $V_{Ti}$, $V_C$, and $V_O$ in the $5 \times 5 \times 1$-Ti$_2$CO$_2$ under biaxial strain are plotted in Figure S5, along with the band structures in Figures S2, S3, S4, S5, S6, and S7. First, it should be noted that magnetism is not noticed even by applying strain on $V_{Ti}$- and $V_O$-Ti$_2$CO$_2$ systems. The effect of strain on the magnetic properties of $V_{C-Ti_2CO_2}$ is discussed in the next section.

Compression and tensile strain tend to decrease the band-gap value of the $V_{O-Ti_2CO_2}$ system, and it remains to be semiconducting; this decrease is more pronounced for compression strain; i.e., the values of band gap continuously decrease from about 1.11 to 0.74 eV under the compression strain from $-3$ to $-7\%$, while the band-gap values are almost unchanged from $-2$ to $+2\%$ and then slightly decrease under tensile strain. The band gap of $V_{O-Ti_2CO_2}$ is sensitive to compression strain more than the tensile one.

More interestingly, compression strain on $V_{Ti}$-Ti$_2$CO$_2$ results in a transition from metal to direct band gap (in the high-symmetry point M). After this transition, the band gap slightly increases to about 0.19 eV for $-7\%$ compression. A detailed view of this electronic nature transition is presented in Figure 6. Also, we notice an overlap of valence and conduction bands (simultaneously crossed by the Fermi level) under tensile strain, and a metallic behavior appears. For equilibrium geometry, $V_{Ti}$-Ti$_2$CO$_2$ embodies semimetallic behavior because valence and conduction bands touch at the Fermi level in the high-symmetry point K. In other words, $V_{Ti}$-Ti$_2$CO$_2$ is very sensitive to any small perturbation to change its electronic nature. In addition, the U term in our calculations (DFTB + U) appears as crucial for the description of delicate changes in the electronic structure (cf. semiconducting behavior when standard PBE-DFT is used).

Moreover, we found that a semiconductor-to-metal transition in $V_{C-Ti_2CO_2}$ can be achieved by applying a compressive biaxial strain. The band gap $E_g$ increases under tensile strain from 0.36 to about 0.53 eV, preserving the $\Gamma$–M direction. Our results suggest that the vacancy defect in Ti$_2$CO$_2$ MXene can be promising for an optical nanodevice by modulating the band-gap properties using strain engineering.

We note that we are not aware of any study that considers the strain effect on both Ti- or C-vacancies. However, A. Bafekry et al.$^{35}$ conducted PBE investigations on the effects of in-plane strain on the electronic properties of the O-vacancy in Ti$_2$CO$_2$ with a 0.81% concentration by considering a periodic slab model. They show that strain engineering can be used to adjust the semiconducting characteristic. In particular, they found that the semiconductor-to-metal transition is achieved by applying a tensile strain over 4% or a compression strain in the range of $-3$ to $-5\%$.

**Effect of C-Vacancy Creation on the Magnetic Properties.** Our calculated results show that among vacancy-defected Ti$_2$CO$_2$ only $V_{C-Ti_2CO_2}$ is FM. Thus, C-vacancy creation can be considered a potential method for achieving magnetism in the Ti$_2$CO$_2$ monolayer. We now focus on analyzing the effect of biaxial strain on the magnetic properties of $V_{C-Ti_2CO_2}$. The variation of the magnetic moments in $V_{C-Ti_2CO_2}$ with respect to compression and tensile strains has been depicted in Figure 7.

Interestingly, a transition from FM semiconducting behavior to NM metallic behavior under negative strain was found. Meanwhile, as the tensile strain increased from 0 to 7%, the magnetic moment varied slowly from 1.95 to 2.00 $\mu_B$, keeping an FM arrangement. This indicates that strain is an effective method for tuning the magnetic moment of Ti$_2$CO$_2$. In fact, as tensile strain increases, the bond lengths of Ti–Ti, Ti–C, and

Figure 6. Detailed view on electronic nature transition under biaxial strain (in the range $-2$, $-1$, 0, 1, and 2%) demonstrated for the band structure of $V_{Ti}$-Ti$_2$CO$_2$ (in the $5 \times 5 \times 1$ supercell). Band structures for a broader range of strains are given in supporting Figures S2 and S3.
Dashed lines are a guide to the eye.

Ti–O slightly increase, which somewhat weakens the covalence interaction between Ti and nearby atoms. Thus, the number of unpaired electrons for Ti atoms also increases. As a result, the magnetic moment of Ti atoms increases.

The spin density distribution is displayed in Figure 8 to visualize the magnetic ordering of V\(_{\text{C}}\)-Ti\(_2\)CO\(_2\). The yellow spherical isosurfaces represent the spin-up electrons, while the blue ones are the spin-down electrons. Clearly, the creation of the C-vacancy in Ti\(_2\)CO\(_2\) is the origin of spin density accumulation around the Ti atoms close to the vacancy. All Ti atoms surrounding the C-vacancy are parallel in spin-up (yellow), verifying the FM ordering in V\(_{\text{C}}\)-Ti\(_2\)CO\(_2\). It is worth noting that the same behavior was found using the DFT + U calculation (see Figure S1).

**Double C-Vacancy Defect in Ti\(_2\)CO\(_2\).** To investigate the change in the electronic structure and the magnetic properties of double C-vacancies in Ti\(_2\)CO\(_2\), spin-polarized band structure calculations were carried out. The second C-vacancy can be created either in the 1st nearest neighbor (1st NN), 2nd nearest neighbor (2nd NN), 3rd nearest neighbor (3rd NN), or 4th nearest neighbor (4th NN) of the existing C-vacancy. A schematic representation of different sites for the second C-vacancy is plotted in Figure S8. We calculated the formation energies and the magnetic energy difference (\(E_{\text{AFM}} - E_{\text{FM}}\)) of these vacancy defects, as listed in Table 3.

![Figure 7.](image) **Figure 7.** (Color online) Variation of magnetic moments of the single C-vacancy on the \(5 \times 5 \times 1\)-Ti\(_2\)CO\(_2\) supercell under biaxial strain. Dashed lines are a guide to the eye.

![Figure 8.](image) **Figure 8.** (Color online) Spin density distribution of the C-vacancy defect on Ti\(_2\)CO\(_2\). The level of the isosurface is \(\pm 0.001\ e/\AA^3\). The yellow and blue hypersurfaces show contours of positive and negative magnetization densities, respectively. The violet color refers to the vacancy.

| 1st NN | 2nd NN | 3rd NN | 4th NN |
|-------|-------|-------|-------|
| \(E_f\) (eV) | 10.04 | 10.55 | 10.40 | 10.56 |
| \(m(\mu_B/\text{cell})\) | 0.37 | 3.11 | 0.06 | 3.30 |
| \(E_{\text{AFM}} - E_{\text{FM}}\) (eV) | 0.04 | 0.20 | 0.07 | 0.21 |
| \(E_g\) (eV) | 0.05 | 0.04\(^\dagger\) | 0.06 | 0.11\(^\dagger\) |

*We note that the spin-down channel behaves significantly different.

According to our calculations, the formation energy when the second C-vacancy is created in the 1st NN is about 0.5 eV lower than the other positions. This difference indicates that the second C-vacancy likes to be created close to the existing one. In addition, an FM alignment was found to be more preferable.

Isovalue surfaces of the spin density distribution (Figure 9) clearly show a spin-polarization around the C-vacancy, and net magnetic moments constructed there from Ti atoms around the C-vacancies have significant magnetization, showing FM coupling. The total magnetic moments and the electronic band-gap values of double C-vacant Ti\(_2\)CO\(_2\) are listed in Table 3. The calculated total magnetic moments are 0.37, 3.11, 0.06, and 3.30 \(\mu_B\) per supercell when the second C-vacancy is created in the 1st NN, 2nd NN, 3rd NN, or 4th NN, respectively. Vacancy creation in the 4th NN increases the net magnetic moments from about 1.95 to 3.30 \(\mu_B\). However, the magnetism is very weak when the second vacancy is created in the 3rd NN position (only about 0.06 \(\mu_B\)).

In addition to ferromagnetism, the energy band gap decreased, keeping the indirect nature upon second C-vacancy formation in different sites. In particular, the system shows a small value of the electronic band gap ranging between 0.04 and 0.11 eV depending on the position of the second C-vacancy. Despite similar indirect gaps, however, the nature of the band structures is very different for 1st NN and 3rd NN vs 2nd NN and 4th NN cases. While the first approach is the nonmagnetic case (both spin channels behave quite similarly), the latter embodies very different gaps in second spin channels, in analogy to half-metal materials (so-called half-semiconductors): the spin-down gaps are \(\approx 1.3\) eV. This is in line with magnetic moments reported in Table 3. A plot of the spin-resolved band structures is shown in Figure S9 for more details. Changing the carrier density by creating a C-vacancy defect in the bare system is a way to tune the electronic and magnetic properties of the system. These results imply that V\(_{\text{C}}\)-Ti\(_2\)CO\(_2\) could be a promising magnetic semiconductor for application in spintronic devices.

**Effect of Strain on the Electronic and Magnetic Properties of Double C-Vacancies.** We now investigate the strain influence on the electronic and magnetic properties of double C-vacancies in Ti\(_2\)CO\(_2\). The band-gap energies and the total magnetic moments of double C-vacancies in Ti\(_2\)CO\(_2\) as a function of biaxial strain are shown in Figure 10.

We found that the electronic band structure is modified significantly under strain, implying that interatomic coupling can
tune the energy band gap. First of all, the tendency of the band gap for the system when the second C-vacancy is created in the 2nd NN is similar to that of the 4th NN under the studied range of strains. In particular, when applying a compression strain, the system shows a metallic behavior. Under tensile strain, the system is initially metallic, and then the gap linearly increases with the increasing tensile strain in the range of +3 to +7%. A maximum gap value of about 0.05 eV can be attained at a tensile strain of 7% for both systems where the second C-vacancy is created either in 2nd NN or in 4th NN. For the system when the second C-vacancy is created in the 1st NN, we found a semiconductor-to-metal transition under a −1% compression strain, and the system remains metallic from −1 to −5% strain, and then it shows semiconductor behavior again at a −6% compression strain. Under tensile strain, the system is an indirect (Γ−M) semiconductor, and the band gap reaches a value of 0.09 eV at 4%. When the second C-vacancy is created in the 3rd NN, the system is an indirect (Γ−M) semiconductor in the range of strain between −7 and +1%, and then a metallic behavior was detected for the tensile strain of 2 and 3%. Under tensile strains of 4, 5, and 6%, the system shows indirect (Γ−M) and (Γ−K) and direct (K−K) semiconducting behavior. In particular, in the strain range of 4−5%, the band gap shows an increasing trend, in which it reaches about 0.18 eV, and it is significantly reduced at 6%. Finally, a semiconductor-to-metal transition was found for a tensile strain of 7%.

Figure 9. (Color online) Spin density distributions of double C-vacancy defect on Ti₂CO₂. (a) 1st NN (isovalue = ±0.001 e/Å³), (b) 2nd NN (isovalue = ±0.001 e/Å³), (c) 3rd NN (isovalue = ±0.0002 e/Å³), and (d) 4th NN (isovalue = ±0.001 e/Å³). The yellow and blue hypersurfaces show contours of positive and negative magnetization densities, respectively. The violet color refers to the vacancies.

Figure 10. (Color online) Electronic band gap and magnetic moments of double C-vacancies in the 5 × 5 × 1-Ti₂CO₂ supercell under biaxial strain. Dashed lines are a guide to the eye.
We have also investigated the effect of biaxial strain on the magnetic properties of a double C-vacancy defect in \( 5 \times 5 \times 1 \) Ti\(_2\)CO\(_2\). In our study, the unstrained V\(_{2C}\)-Ti\(_2\)CO\(_2\) is predicted to be FM. Moreover, we show that there is no transition from the FM alignment was found for all structures by applying biaxial strain in the range of \(-7\) to \(+7\%\). For the system with a second C-vacancy in the 1st NN under biaxial strain, the net magnetic moment is enhanced from 0.05 to 1.51 \( \mu_B \) from \(-7\) to \(-5\%\) strain and then it decreases to a small value of about 0.02 \( \mu_B \) from a strain range between 1 and \( +7\%\). We reported that in the system when the second C-vacancy is created in the 2nd NN, the magnetic moment is small and then it increases with the increase of the strain from \(-4\%\) except for 1 and \( +2\%\), where it is slightly decreased. Interestingly, if the strain is increased to \( +7\%\), the net magnetic moment can reach as high as 3.92 \( \mu_B \). In addition, the net magnetic moment of the structure with the second C-vacancy at 3rd NN is greatly enhanced under tensile strain. Note that a maximum value of 2.02 \( \mu_B \) is found for a strain of \( +6\%\). The compression strain, on the other hand, reduces the net moment from 0.06 to 0.01 \( \mu_B \) when the strain is beyond \(-6\%\). For the system with the second C-vacancy in the 4th NN under biaxial strain, the magnetic moment is small, and then it decreases to a small value of about 0.02 \( \mu_B \) at a \( +7\%\) tensile strain. As a result, applying biaxial strain is an effective way to regulate the electronic and magnetic properties of double C-vacancies in Ti\(_2\)CO\(_2\).

Combination of Single Vacancies. Different kinds of mixed defects could occur in 2D materials.\(^{102}\) Therefore, we investigate other types of mixed defects, i.e., V\(_{1TiC}\)-Ti\(_2\)CO\(_2\) (1 Ti monovacancy + 1 C monovacancy) and V\(_{1TiO}\)-Ti\(_2\)CO\(_2\) (1 Ti monovacancy + 1 O monovacancy). We found that both nonstrained V\(_{1TiC}\)-Ti\(_2\)CO\(_2\) and V\(_{1TiO}\)-Ti\(_2\)CO\(_2\) show metallic character. In Figure 11, we plot the variation of the energy band gap as a function of biaxial strain, which corresponds to the variation of the electronic band structures under strain (which are plotted in supplementary Figures S12 and S13). By applying a strain in the range from \(-7\) to \(+7\%\), V\(_{1TiC}\)-Ti\(_2\)CO\(_2\) kept its metallic behavior (please see Figures S14 and S15). For the V\(_{1TiO}\)-Ti\(_2\)CO\(_2\) system, there is a metal-to-indirect (\( \Gamma-M \)) semiconductor transition under biaxial tensile strain. The band gap changes from about 0.07 to 0.28 eV, with the strain from \(+1\) to \( +7\%\). Moreover, upon biaxial tensile strain, no transition occurs, and the system remains metallic. It is worth noting that for both systems, we found that the structures show no magnetism for all ranges of strain between \(-7\) and \(+7\%\).

CONCLUSIONS
In the present work, we have studied the structural, electronic, and magnetic properties of a Ti\(_2\)CO\(_2\) monolayer in the presence of Ti-, C-, or O-vacancy defects and/or under biaxial strain via the DFTB+U method. We found that a C-vacancy is energetically more stable than Ti- and O-vacancies. The introduction of a single Ti-vacancy on a \( 5 \times 5 \times 1 \) supercell makes the system undergo a semiconductor-to-metal transition, and the vacancy enhances the electronic conductivity. While semiconducting Ti\(_2\)CO\(_2\) can be metalized by a Ti-vacancy, the band-gap values range from 0.36 to 1.12 eV upon C- and O-vacancy creation, respectively. We also found that Ti- and O-vacancies do not induce any magnetization in the system, but the magnetism of the 1.95 \( \mu_B \)/cell is induced by a single C-vacancy in Ti\(_2\)CO\(_2\). This was never observed in any previous DFT calculation; the U term appears as crucial. We proved that standard GGA-DFT fails in the right description of the ground magnetic properties of Ti\(_2\)CO\(_2\) MXene by comparison to DFT + U and hybrid DFT calculations and showed our DFTB + U results as correct.

Furthermore, we investigated the effects of biaxial strain on V\(_{1TiV}\), V\(_{1CO}\), and V\(_{1O}\)-Ti\(_2\)CO\(_2\). The semiconductor behavior is well preserved under both compression and tensile strained V\(_{1TiV}\)-Ti\(_2\)CO\(_2\). Semiconducting characteristics on V\(_{1CO}\)-Ti\(_2\)CO\(_2\) under tensile strain were converted to metallic characteristics under compression strain. In addition, it loses magnetization with compression strain, whereas it remains an FM semiconductor with positive biaxial strain reaching about 2 \( \mu_B \) per unit cell. Moreover, metal-to-direct (\( M-M \)) semiconducting phase transition occurred under negative strain in the case of the V\(_{1TiO}\)-Ti\(_2\)CO\(_2\) system. It is worth noting that no magnetism is found for Ti\(_2\)CO\(_2\) in the presence of Ti- or O-vacancies or under strain in our computation. After the second C-vacancy creation, magnetic states are maintained, and depending on the position, the electronic band gap decreases to a value between 0.04 and 0.11 eV. Ti\(_2\)CO\(_2\) attains a net magnetic moment of 3.30 \( \mu_B \) through the creation of a second C-vacancy at the 4th NN position.

Modulation of the band gap using strain engineering suggests that the defected fully O-functionalized Ti\(_2\)CO\(_2\) is a potential candidate for the design of novel optoelectronic devices. This work provides encouraging results for the vacancy and strain-tunable electronic and magnetic behavior in Ti\(_2\)CO\(_2\).

ASSOCIATED CONTENT
Supporting Information
The Supporting Information is free of charge at https://pubs.acs.org/doi/10.1021/acsomega.2c05037.

DFT calculations of the spin density of the C-vacancy in Ti\(_2\)CO\(_2\), band structures of V\(_{1TiV}\), V\(_{1CO}\), and V\(_{1O}\)-Ti\(_2\)CO\(_2\) under biaxial strain; double C-vacancies in Ti\(_2\)CO\(_2\); MD calculations under \( \pm 7\% \) strain, and band structures of V\(_{1TiV}\) and V\(_{1TiO}\) under biaxial strain (PDF)
Author Contributions
This manuscript was written through the contributions of both authors. Both authors have given their approval to the final version of the manuscript.

Notes
The authors declare no competing financial interest.

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