Strain-Induced Band Modulation, Work Function, and QTAIM Analysis of Surface O-Functionalized Ti₂C MXene

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ABSTRACT: Functionalized MXenes have wide applications in the fields of gas sensors, thermoelectric materials, and hydrogen storage. Strain-induced band engineering and the work function (WF) of Ti₂CO₂ MXene are investigated theoretically. The calculations reveal that Ti₂CO₂ MXenes are stable because of the negative $E_{coh}$ and all the strains considered are within the elastic limit. For Ti₂CO₂ MXene, strain-induced blue shift of the Ti d state results in the transformation from a semiconductor to a metal. At about 4%, Ti₂CO₂ MXene transforms from an indirect band gap to a direct band gap. The decreased WF induced by the strain improves the power efficiency of Ti₂CO₂ MXene.

1. INTRODUCTION

Lithium-ion batteries (LIBs) have been the most important and efficient energy storage devices because of their commercialization and are widely applied to smart grids.¹ However, the applications of LIBs have been hindered by safety issues such as overcharge, thermal runaway, lithium dendrites, and so on. In addition, the high cost of LIBs is another factor that hinders their application. Two-dimensional (2D) materials such as layered materials, graphene, and so on²⁻⁵ have been explored in detail because of their potential application in LIBs. Because of the unique structure, these layered materials have excellent properties such as thermal properties, variable band gap, and so forth.⁶⁻⁹ For graphene, the limited range of the band gap hinders its application in the field of nanoelectronics, etc. In addition, the carbon network and the high cost of graphene further impeded its application. Therefore, extensive works are continued to design photodetectors and search for new layered materials with a wide band gap and good thermal stability.

2D materials with a general formula of $M_nX_{n-1}$ (MXenes), where $n = 1−4$, have outstanding properties and are extensively used in battery electrode materials¹⁰⁻¹¹. MXene nanosheets can be obtained from MAX materials, which we have discussed before.¹¹ In this process, some functionalized groups such as F, O, and/or OH are on the surface of the monolayer, which results in the formation of functionalized MXenes (denoted $M_{n+1}(X_nT_x)$). Here, $T$ represents the functionalized groups F, O, and/or OH and $x$ is the termination number.¹³

To date, more than 70 of the MAX compounds are synthesized,¹⁴ while the synthesized MXenes are severely scarce. Among all potential MXene phases, Ti₂C has the biggest superficial area per weight and is one of the most potential electrode materials. Guo et al.¹⁵ investigated the stress–strain curves of Ti₂C and the deformation mechanism theoretically. They thought that 2D Ti₂C is less stiff than graphene but stiffer than MoS₂. In addition, they also thought that the terminating O-functional groups on the 2D Ti₂C surface can improve the mechanical properties.¹⁵ Gao et al.¹⁶ theoretically explored the adsorption behavior of mercury on Ti₂CO₂. Ti₂CO₂ is a semiconducting feature with superhigh carrier mobility¹⁷⁻²⁰ and thermal stability.²¹ It has the band gap of 0.26 eV based on density functional theory (DFT).²² The hole mobility of Ti₂CO₂ is the highest among the semiconducting MXenes²³ and its thermal conductivity is 21.9 W m⁻¹ K⁻¹ at room temperature, so Ti₂CO₂ MXene can be considered as a thermoelectric material or gas sensor. In addition, Ti₂CO₂ is also widely applied in energy storage²⁴ and wastewater treatment.²⁵

Work function (WF) has an important role in field-effect transistors.²⁶⁻²⁷ Materials with low WFs can improve the power efficiency. The strain or electric field can modulate the WFs, which is important to maximize the performances of the
device. Until now, the modulation of Ti$_2$CO$_2$ under strain is not available.

Structural variation can affect the properties of 2D materials. Applying strain or vacancy defect can tune the band gap of MXenes, which is desired in technological applications. In this paper, the band gap and WF are modulated by biaxial strain which is desired in industrial applications, and the electronic structure and the magnetism mechanism of Ti$_2$CO$_2$ are investigated further. The comparison of the related properties between Ti$_2$CO$_2$ and similar 2D materials and the analysis of Bader's quantum theory of atoms in molecules (QTAIM) for Ti$_2$CO$_2$ are performed in our paper, which is not available in previous works. Our investigation will provide useful information to modulate the physical and chemical properties of MXenes.

2. RESULTS AND DISCUSSION

2.1. Structural Properties. Figure 1a presents the structures of the Ti$_2$AlC MAX phase and Ti$_2$CO$_2$ MXene.

![Figure 1](https://example.com/figure1.png)

Figure 1. Atomic structure as ball-and-stick models. (a) Ti$_2$AlC MAX phase; (b) Ti$_2$CO$_2$ monolayer top view; and (c) Ti$_2$CO$_2$ monolayer side view.

Previous research studies indicate that the energetically most stable structure is that the O atom is at the position of etched away Al atoms. Mechanical strain is an effective approach to modulate the electronic structure. The schematic illustration of the biaxial strain is shown in Figure 1b. In our paper, the strain is set as $e = [(a - a_0)/a_0] \times 100\%$, where $a_0$ is the lattice parameter without strain and $a$ is the lattice parameter with strain. Figure 1b also denotes the supercell by a dashed line frame, and the supercell size is 6.0596 Å. Figure 1c presents the Ti$_2$CO$_2$ monolayer from the side view.

Cohesive energy ($E_{coh}$) can be used to understand the phase stability. For Ti$_2$CO$_2$, $E_{coh}$ is generated by eq 1.

$$E_{coh} = \frac{E_{tot}(\text{Ti}_2\text{CO}_2) - 2E_{\text{atm}}(\text{Ti}) - E_{\text{atm}}(\text{C}) - 2E_{\text{atm}}(\text{O})}{5}$$

where $E_{tot}$ is the total energy of Ti$_2$CO$_2$ with strain and $E_{atm}$ represents the energies of three single atoms. Negative $E_{coh}$ indicates the stable crystal structure.

Table 1 lists the $E_{coh}$ for Ti$_2$CO$_2$ with strain from $-5\%$ to $+5\%$. In Table 1, negative $E_{coh}$ indicates the stable structure of Ti$_2$CO$_2$ under strain.

2.2. Band Gap Modulation by Strain. Ti$_2$CO$_2$ MXene without strain is a semiconductor with an indirect band gap, which interrupts efficient light emission and hinders its application in optical devices. No magnetism is found for Ti$_2$CO$_2$ under strain in our computation. The band gap of Ti$_2$CO$_2$ without strain is 0.256 eV, which is smaller than those of Sc$_2$CF$_2$ (1.023 eV) and MoS$_2$ (1.76 eV).

Figure 2 presents the band structure of Ti$_2$CO$_2$ under strain. The indirect band gap for Ti$_2$CO$_2$ MXene is the valence band maximum (VBM) at the $\Gamma$ point and the conduction band minimum (CBM) at the M point. From Figure 2, the indirect band gap from M to $\Gamma$ point decreases with strain from $-1\%$ to $-3\%$. Moreover, Ti$_2$CO$_2$ undergoes semiconductor-to-metal transformation with the strain larger than $-3\%$. The band gap increases with the strain from 0% to 5%. There is an $\Gamma$ to $\Gamma$ indirect band gap with the strain from 1% to 3% and a $\Gamma$ to M direct band gap with the strain larger than 3%. From Figure 2, the $\Gamma$ to $\Gamma$ direct band gap is not so sensitive to the strain. The band gap of Ti$_2$CO$_2$ changes from 0.256 to 0.449 eV with the strain from 0% to 5%. Therefore, the transformation from an indirect to a direct band gap for Ti$_2$CO$_2$ enables it to have potential applications in fields such as thermoelectric materials and so on.

The strain energy is explored to check whether the strain considered is within the elastic limit. Strain energy $E_s = (E_{\text{strained}} - E_{\text{unstrained}})/n$, with $n$ being the number of atoms in the unit cell. Figure 3 presents the $E_s$ and the band gap under strain. The characteristic of the quadratic function of the strain–energy curve indicates that all the strains considered are within the elastic range of Ti$_2$CO$_2$ and are fully reversible. From Figure 3, the band gap is maximum (~0.449 eV) under 4% strain. At about $-3\%$ strain, Ti$_2$CO$_2$ goes from a semiconductor to a metal.

![Figure 2](https://example.com/figure2.png)

Figure 2 presents the direct and indirect band gaps between $\Gamma$ and M points for Ti$_2$CO$_2$ under strain. The energy difference between $\Gamma \rightarrow \Gamma$ and $\Gamma \rightarrow M$ band gaps is 0.006 eV at 4% strain. Therefore, 4% strain is the critical point at which Ti$_2$CO$_2$ transforms from an indirect to a direct band gap.

The contribution of each atom to the energy level (EL) is investigated in order to confirm which factor mainly affects the band gap and plotted in Figure 5. We consider two Ti (Ti$_1$ and Ti$_2$) atoms, two O (O$_1$ and O$_2$) atoms, and a C atom. For Ti$_2$CO$_2$ without strain, C, 2Ti, and 2O atoms contribute 39.58, 28.7, and 31.7% to the EL at the VBM, respectively. 2Ti and 2O atoms contribute 48.7% and 33.7% to the EL at the CBM, respectively. Ti$_2$CO$_2$ with $+5\%$ strain has a $\Gamma \rightarrow \Gamma$ direct band gap. The C, 2Ti, and 2O atoms contribute 38.9% (28.6%).
30.6% (37.7%), and 30.5% (33.6) to the EL at the VBM (CBM), respectively.

Figure 6 presents the partial density of states (PDOS) under strain. The dotted vertical lines in Figure 6 indicate the Fermi level. Ti d and O p have the strong hybridization in the energy range of −6 to −4 eV for Ti$_2$CO$_2$ without strain. The peaks around −2 eV mainly originate from the Ti d, O p, and C p states. The Ti d state provides the main contribution for the peak at 2.5 eV. Ti$_2$CO$_2$ without strain is a semiconductor. The Ti d state undergoes a red shift with the increase in the compression strain and across the Fermi level at −3% strain. The Ti d state undergoes a blue shift with the increase of tensile strain, resulting in the increase of the band gap.

Figure 7 plots the PDOS of each atom of Ti$_2$CO$_2$ with strain. From Figure 7, it can be observed that for Ti$_2$CO$_2$ without strain, Ti d mainly contribute to the CBM state (M

![Figure 2. (a–f) Band gap of Ti$_2$CO$_2$ under biaxial strain.](image_url)

![Figure 3. Band gap and strain energy of Ti$_2$CO$_2$ MXene under strain.](image_url)

![Figure 4. Direct and indirect band gaps between Γ and M points under strain.](image_url)
2.3. WF Engineering by Strain. WF is an important physical parameter of materials and plays a significant role in light-emitting diodes and field effect transistors. WF, \( \phi \), is defined as the energy required to promote an electron from the Fermi EL to vacuum: \( \phi = E_F - E_0 \), where \( E_0 \) and \( E_F \) are the potential in the vacuum and the Fermi level, respectively.

Figure 8 presents the WFs of \( \text{Ti}_2\text{CO}_2 \) under strain. The WF of \( \text{Ti}_2\text{CO}_2 \) without strain is 5.90 eV, which is close to the results of Khazaei et al.\(^{40} \) but larger than that of \( \text{Sc}_2\text{CF}_2 \) (4.803 eV)\(^{39}\) and the graphene/black phosphorene bilayer (5.38 eV).\(^{41} \) The WF decreases gradually with the increase of tensile strain and is 5.72 eV at +5% strain. This indicates that strain can modulate the WF effectively. For \( \text{Ti}_2\text{CO}_2 \) MXene, increasing tensile strain can improve the catalytic activity of materials.

According to the report of Ma et al.,\(^{42} \) \( \text{Ti}_2\text{CO}_2 \) under compressive strain has a higher WF, which can reduce the Schottky barrier and decrease the field emission performance. \( \text{Ti}_2\text{CO}_2 \) under tensile strain has a lower WF, which can improve the field emission performance. \( \text{Ti}_2\text{CO}_2 \) under +5% strain has a better field emission performance, while \( \text{Ti}_2\text{CO}_2 \) under −5% strain has a poor field emission performance. On the other hand, \( \text{Ti}_2\text{CO}_2 \) under tensile strain can be treated as a cathode because of the lower WF, while \( \text{Ti}_2\text{CO}_2 \) under compressive strain can be considered as an anode because of the higher WF.

2.4. Migration Mechanism of the Carrier. In order to get a deep insight into the electronic distribution, the electron localization function (ELF) for the \( \text{Ti}_2\text{CO}_2 \) monolayer is investigated. The ELF can measure the probability of finding an electron with the same spin. The ELF ranges from 0 to 1. ELF = 1 indicates perfect localization, ELF = 0.5 indicates the metallic bond, while ELF = 0 indicates delocalization. Here, we only list the ELF without strain and with +5 and −5% strain along the y-direction (shown in Figure 1), in Figure 9.

From Figure 9, it can be observed that there exist strong Ti–O and Ti–C interactions under 0, +5, and −5% strain. The ELF values around the O and C sites are larger than the EFL value around the Ti site. Therefore, there exist partially covalent bonds between Ti and O and Ti and C atoms.

Spatial charge distributions are also explored in our study. Figure 10 exhibits the partial charge distribution of the CBM and the VBM of \( \text{Ti}_2\text{CO}_2 \) without strain and with +5% strain. The VBM are located around C and O atoms, whereas most of the charge shifts to the Ti atom in the CBM state for \( \text{Ti}_2\text{CO}_2 \) without strain. For \( \text{Ti}_2\text{CO}_2 \) with +5% strain, the distribution of the VBM is same as that without strain. In the CBM state, most of the charge shifts to the Ti atom and a little shifts to the O atom. This analysis is in accordance with the result of PDOS of \( \text{Ti}_2\text{CO}_2 \). The different CBM and VBM distributions can inhibit the recombination of electron–hole pairs.

From Bader analysis, the charges of each of the O, Ti, and C atoms under strain are −1.2518, +2.2504, and −1.9944 e\(^{−} \), respectively. (The numbers of valence electrons employed in the calculations for O, Ti, and C atoms are 6, 4, and 4, respectively.) The charges of each of the O, Ti, and C atoms with +5% strain are −1.3201, +2.3668, and −2.0935 e\(^{−} \), respectively. For O, Ti, and C atoms with −5% strain, the charges are −1.3087, 2.4188, and −2.2211 e\(^{−} \), respectively. Each of the O and C atoms gains more electrons from the Ti atom with the increase of the strain, which indicates that there exists enhanced bonding.

2.5. Quantum Theory of Atoms in Molecules. Bader’s QTAIM can confirm the chemical bonding in a molecule. Li et al.\(^{43} \) described the QTAIM analysis in detail. \( \rho(r) > 0 \) and \( \nabla^2\rho < 0 \) indicate the predominant covalent interaction, while small \( \rho(r) \) and \( \nabla^2\rho > 0 \) indicate the ionic interaction. The total energy density component at a bond critical point (BCP), \( H(r) \), is equal to the sum of the local electron potential energy density \( V(r) \) and the electron kinetic energy density \( G(r) \).

\[ \xi = \frac{|V(r)|}{G(r)} \quad \begin{cases} \xi < 1 \text{ ionic bond type} \\ \xi > 2 \text{ covalent bond type} \\ 1 < \xi < 2 \text{ intermediate bond type} \end{cases} \]

(2)

The ratio \( \xi \) can also be used to reveal the nature of atomic interactions. From Table 2, it can be seen that \( \xi \) under strain is larger than 1 and less than 2 for the listed bonds, which indicates that all listed bonds (Ti–O and Ti–C) have the intermediate character. Table 2 also lists the other parameters such as the three curvatures (\( \lambda_1, \lambda_2, \text{ and } \lambda_3 \) of the electronic density and so forth.

3. CONCLUSIONS

In this paper, the electronic properties and WF of monolayered \( \text{Ti}_2\text{CO}_2 \) under strain are investigated based on first-principles calculations. The negative \( E_{\text{coh}} \) indicates the stability of \( \text{Ti}_2\text{CO}_2 \).
Ti$_2$CO$_2$ undergoes the semiconductor-to-metal transformation under $\pm 3\%$ strain, which results from the red shift of the Ti d state. Ti$_2$CO$_2$ undergoes an indirect→direct transformation of the band gap under strain larger than $+3\%$ because of the blue shift of the Ti d state. The band gap of Ti$_2$CO$_2$ increases from 0.256 to 0.449 eV in the strain range of 0 to 5%. The critical point with an indirect-to-direct gap is 4%. Increasing the tensile strain can improve the power efficiency of materials for Ti$_2$CO$_2$ MXene. The charge analysis indicates that each of the O and C atoms gains more electrons from the Ti atom with increasing strain, which indicates that there exists a strong intermediate bonding and is further confirmed by the analysis of QTAIM.

4. COMPUTATIONAL DETAILS

First-principles calculations were performed by DFT implemented in the Vienna ab initio simulation package (VASP). The projector-augmented wave (PAW) method was used to describe the interactions between the valence electrons and ionic cores. The exchange–correlation energy was treated within the generalized gradient approximation using the Perdew–Burke–Ernzerhof functional. The pseudopotentials utilized the valence state of 3d$^2$4s$^1$, 2s$^2$2p$^2$, and 2s$^2$2p$^4$ for Ti, C, and O, respectively. A vacuum space of 25 Å was used in the z-direction to avoid the interaction. The Brillouin zone was sampled by using a 12 $\times$ 12 $\times$ 1 $k$-mesh according to the Monkhorst–Pack method. The spin polarization is consid-
The van der Waals (vdW) interaction is taken into consideration by using the semiempirical correction of Grimme (DFT-D3). The energy cutoff of the plane waves was set to 700 eV. The positions of atoms were fully optimized, and the energy converged threshold was $10^{-6}$ eV per atom, and 0.05 eV/Å in force. A denser $25 \times 25 \times 1$ mesh is used to calculate the electronic density of states.

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**Notes**

The authors declare no competing financial interest.

**Acknowledgments**

This work was supported by the Program for Science & Technology Innovation Talents in Universities of Henan Province (No 14HASTIT039) and the Innovation Team of Henan University of Science and Technology (2015XTD001).

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### Table 2: Position and Properties of Ti$_3$C$_2$O$_2$, Electron Density BCP

| Bond  | Position | ρ(σ)/e Å$^{-3}$ | V(σ)/e Å$^{-3}$ | H(σ)/e Å$^{-3}$ | Intraatomic Indices |
|-------|----------|----------------|----------------|----------------|-------------------|
| Ti(1)–O(1) | (0.0399, 0.5041, 0.5960) | 0.0393 | 0.0453 | 0.0512 | |
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