Large-Gap Two-Dimensional Topological Insulator in Oxygen Functionalized MXene

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Abstract

Two-dimensional (2D) topological insulator (TI) have been recognized as a new class of quantum state of matter. They are distinguished from normal 2D insulators with their nontrivial bandstructure topology identified by the $Z_2$ number as protected by time-reversal symmetry (TRS). 2D TIs have intriguing spin-velocity locked conducting edge states and insulating properties in the bulk. In the edge states, the electrons with opposite spins propagate in opposite directions and the backscattering is fully prohibited when the TRS is conserved. This leads to quantized dissipationless “two-lane highway” for charge and spin transportation and promises potential applications. Up to now, only very few 2D systems have been discovered to possess this property. The lack of suitable material obstructs the further study and application. Here, by using first-principles calculations, we propose that the functionalized MXene with oxygen, $M_2CO_2$ (M=W, Mo and Cr), are 2D TIs with the largest gap of 0.194 eV in W case. They are dynamically stable and natively antioxidant. Most importantly, they are very likely to be easily synthesized by recent developed selective chemical etching of transition-metal carbides (MAX phase). This will pave the way to tremendous applications of 2D TIs, such as “ideal” conducting wire, multifunctional spintronic device, and the realization of topological superconductivity and Majorana modes for quantum computing.
I. INTRODUCTION

The field of topological insulator (TI) started from the theoretical proposal of two-dimensional (2D) TI state in graphene.\textsuperscript{1–3} Though the band gap of graphene is too tiny to be observed,\textsuperscript{2} the conceptual achievement in the band topology has opened the door to the field of topological quantum states (TQSs).\textsuperscript{9,10} The theoretical proposal\textsuperscript{3} and experimental verification\textsuperscript{9} of 2D TI in quantum well of HgTe/CdTe have boosted the quick rising of the field of TIs. The idea of band topology has been extended to 3D system\textsuperscript{10–12} and other symmetry protected TQSs.\textsuperscript{13} Recently, the band topology in metals, including the topological Dirac semimetal\textsuperscript{14–17} Weyl semimetal\textsuperscript{18–23} and Node-line semimetal\textsuperscript{24–27} has also been intensively studied. Many of the material realization of these TQSs are firstly predicted by theoretical calculations and then confirmed by experimental observations.\textsuperscript{7,28} The bulk-boundary correspondence of the topological matters is well known now and it is one of the most unique properties of them. For example, 2D TI is expected to host quantum spin Hall effect (QSHE) with 1D helical edge states, namely the electrons in such edge states have opposite velocities in opposite spin channels. Thus, the backscattering is prohibited as long as the perturbation does not break the time-reversal symmetry (TRS). Such helical edge states are expected to serve as “two-lane highway” for dissipationless electron transport, which promises great potential application in low-power and multi-functional spintronic devices. Large band gap 2D TI is also crucial to realize the long-sought-for topological superconductivity and Majorana modes through proximity effect.\textsuperscript{6,29} In this point of view, 2D TI is more preferred than 3D one, where the backscattering in the surface states is not fully prohibited.

Compared with the number of well characterized 3D TI materials, fewer 2D TIs have been experimentally discovered.\textsuperscript{6,30} The quantum wells of HgTe/CdTe\textsuperscript{9} and InAs/GaSb\textsuperscript{31} are among the well-known experimentally confirmed 2D TIs. Both of them require precisely controlled MBE growth and operate at ultra-low temperature. These experimental conditions make further studies hard and reduces the possible applications. There have been many efforts to find “good” 2D TIs, which are expected to have the following advantages: (1) being easy to be prepared; (2) having large bulk band gap to be operated under room temperature or higher; (3) being chemically stable upon exposure to air; (4) being composed of cheap and nontoxic elements. The theoretical attempts for predicting good TIs can be roughly classified into two categories. 1) tuning the strength of spin-orbit coupling (SOC),
i.e., the band gap, based on graphene-like honeycomb lattice, such as the low-buckled silicene\textsuperscript{32}, chemically decorated single layer honeycomb lattice of Sn\textsuperscript{32}, Ge\textsuperscript{33} and Bi or Sb\textsuperscript{35} and bucked square lattice BiF\textsuperscript{36}. 2) examining new 2D systems, which might be exfoliated from the 3D layered structural materials, such as ZrTe\textsubscript{5}, HfTe\textsubscript{5}\textsuperscript{37} and Bi\textsubscript{4}Br\textsubscript{4}\textsuperscript{38}. Transition-metal dichalcogenide (TMD) in 1T\textsuperscript{39} and square-octagon haackelite\textsuperscript{40–42} structure also belong to the later category. None of the above has been confirmed by experiments yet, though ZrTe\textsubscript{5}, HfTe\textsubscript{5} and Bi\textsubscript{4}Br\textsubscript{4} seem to be very promising, since they do exist experimentally and and their single layers are TIs without any additional tuning.

Regarding oxide materials, none of them is known to be TI in the experiment, though there are several theoretical proposals available in the literatures, e.g., 2D TI in single layer of iridate Na\textsubscript{2}IrO\textsubscript{3}\textsuperscript{43} topological Mott insulator\textsuperscript{44} and Weyl semimetal in pychorelcore A\textsubscript{2}Ir\textsubscript{2}O\textsubscript{7}\textsuperscript{18} axion insulator in spinnel Osmate\textsuperscript{45} and 3D TI in perovskite of YBiO\textsubscript{3}\textsuperscript{46} and heavily doped BaBiO\textsubscript{3}\textsuperscript{47}. It is generally believed that the strong electronegativity of oxygen leads to full ionization of cations and results in ionic bonds with large band gap, which makes band inversion difficult. However, the noticeable advantages of oxygen compounds, i.e., naturally antioxidant and stable upon exposure to air, have stimulated continuous efforts in searching for new oxide TIs.

In this paper, by using first-principles calculations we demonstrate that the functionalized MXenes\textsuperscript{48–50} with oxygen, M\textsubscript{2}CO\textsubscript{2} with M=W, Mo and Cr, are 2D TIs. Our phonon calculations indicate that the crystal structures are dynamically stable. The band inversion, which is crucial to the nontrivial band topology, is found to occur among the bonding and anti-bonding states of M \textit{d}-orbitals. The results are robust against the use of different exchange-correlation functional approximations. The bulk band gap of W\textsubscript{2}CO\textsubscript{2} is as large as 0.194 eV within generalized gradient approximation (GGA) and is enhanced to 0.472 eV within hybrid functional (HSE06).\textsuperscript{51,52} Its Z\textsubscript{2} invariant is 1 and has conducting helical edge states. Recently, the 2D material MXene have been successfully obtained by the selective chemical etching of MAX phases — M\textsubscript{n+1}AX\textsubscript{n} (n=1, 2, 3, ...), where M, A and X are a transition metal, an element of group 12-14, C or N, respectively.\textsuperscript{53} The bare surfaces of MXene sheet are chemically active and are usually terminated by some atoms or chemical groups depending on the synthesis process, which are usually fluorine (F), oxygen (O), or hydroxyl (OH).\textsuperscript{54–56} Therefore, we believe that our proposed M\textsubscript{2}CO\textsubscript{2} can be probably realized experimentally in the future and thus, will advance the application of TI greatly.
TABLE I: The total energies (in eV per unit cell) for the six possible configurations of W$_2$CO$_2$, Mo$_2$CO$_2$ and Cr$_2$CO$_2$. For each configuration, the structure is fully relaxed. In each unit cell, two oxygen atoms are required for full surface saturations. The symbols T, A, and B indicate three different absorption sites of oxygen atoms as depicted in Fig. 1. All calculations here are performed without spin polarization and within GGA.

| sites of Oxygen | W$_2$CO$_2$ | Mo$_2$CO$_2$ | Cr$_2$CO$_2$ |
|----------------|-------------|-------------|-------------|
| TT             | 3.162       | 2.779       | 1.790       |
| AA             | 1.189       | 1.112       | 0.618       |
| TB             | 1.828       | 1.782       | 1.370       |
| TA             | 2.024       | 1.733       | 1.034       |
| BB             | 0.00        | 0.00        | 0.00        |
| BA             | 0.878       | 0.698       | 0.329       |

II. COMPUTATIONAL DETAILS

First-principles calculations were carried out by using the Vienna \textit{ab initio} simulation package (VASP$^{57,58}$). Exchange-correlation potential was treated within the generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof type$^{59}$ SOC was taken into account self-consistently. The cut-off energy for plane wave expansion is 500 eV and the k-point sampling grid in the self-consistent process was 12×12×1. The crystal structures have been fully relaxed until the residual forces on each atom becomes less than 0.001 eV/Å. A vacuum of 20 Å between layers was considered in order to minimize the interactions between the layer with its periodic images. PHONOPY has been employed to calculate the phonon dispersion$^{60}$. Considering the possible underestimation of band gap within GGA, non-local Heyd-Scuseria-Ernzerhof (HSE06) hybrid functional$^{51,52}$ is further supplemented to check the band topology. To explore the edge states, we apply the Green’s function method$^7$ based on the tight-binding model with the maximally localized Wannier functions (MLWF)$^{61,62}$ of $d$ orbitals of M and $p$ orbitals of C and O as basis set. MLWF are generated by using the software package OpenMX$^{63,64}$. 


FIG. 1: (Color online) (a) Top view and (b) side view of optimized crystal structure of \( \text{W}_2\text{CO}_2 \) and its 2D Brillouin zone. There are three possible sites for oxygen decoration on either side of the surface, namely B (on top of C site), T (on top of W in top surface), A (on top of W in bottom surface). (c) The triangular prism formed by O and C ions surrounds W. (d) The phonon spectrum for optimized \( \text{W}_2\text{CO}_2 \).

III. RESULTS AND DISCUSSION

The crystal structure of oxygen functionalized MXene is shown in Fig. 1. Bare MXene \( \text{M}_2\text{C} \) is basically a three-layer structure with trigonal lattice. The C atoms form a layer, which is sandwiched between two M layers. The in-plane sites of M atoms are \((1/3, 2/3)\) and \((2/3, 1/3)\), respectively, of the trigonal lattice of C atoms. The bare surfaces of MXene sheet are basically terminated by M atoms and they are chemically reactive. Usually, the surfaces are terminated by F, O or OH depending on the synthesis process. This brings a chance to
tune the electronic properties of MXene by appropriate surface functionalization. It has previously been shown that the MXenes with the full surface functionalizations are thermodynamically more favorable than the partial functionalizations, where the full surface functionalization requires two chemical groups per cell. As shown in Fig. 1, the oxygen atom might occupy three different sites on the surface, namely A, B and T on each surface. Therefore, there are totally six combinations for decoration of two surfaces as listed in Table. For each case, the crystal structure is fully relaxed and the results of total energy calculations are summarized in Table. It is observed that the MXene with BB-type oxygen functionalization obtain the lowest energy. In this configuration the M atom sits inside of a trigonal prism formed by the surrounding C and O, which is very similar to Mo atom in 1H structure of MoS$_2$. The phonon spectrum of the energetically stable crystal structure is calculated and shown in Fig. (d). Obviously, there is no imaginary frequency, which means such structures are also dynamically stable.

The electronic band structure of W$_2$CO$_2$ is shown in Fig. 2. It is found that there is a degenerate band touch point on the Fermi level when SOC is not considered. These degenerate states are mostly composed of $d_{x^2-y^2}$ and $d_{xy}$ orbitals of W atoms as shown by the fat-band analysis. If SOC is further considered, it becomes an insulator. Since it has inversion symmetry, the parity configuration of occupied bands at four time-reversal invariant momenta in the 2D BZ can be easily obtained and the $Z_2$ invariant is found to be 1. This indicates that W$_2$CO$_2$ is a 2D topological insulator with an indirect band gap as large as 0.194 eV. The topologically protected conducting edge states have Dirac cone like dispersion and connect the bulk valence and conduction bands.

The total and projected partial density of states, as well as the fat-band plot, clearly show that around Fermi level the W $d$ orbitals are dominant around the Fermi level. The $p$ orbitals of C and O are mainly located -2 eV below the Fermi level. The five $d$ orbitals of W atom are within the triangular prism crystal field of $C_{3v}$ symmetry. The $d_{xz}$ and $d_{yz}$ orbitals are double degenerate and are higher in energy due to the strong hybridization with the $p$ orbitals of C and O. The $d_{x^2-y^2}$ and $d_{xy}$ orbitals are also degenerate and they are around the Fermi level. The $d_{z^2}$ orbital has quite weak hybridization with ligand elements since it points to the center of the ligand triangle. It is also around the Fermi level and slightly lower than $d_{x^2-y^2}+d_{xy}$. Therefore, in order to uncover the low-energy physics of W$_2$CO$_2$, we just need to take into account three three $d$ orbitals, $d_{x^2-y^2}$, $d_{xy}$ and $d_{z^2}$, of the
FIG. 2: (Color online) Band structure for W$_2$CO$_2$ calculated (a) without and (b) with spin-orbit coupling (SOC). The fat-band are scaled with the projected weight of different atomic orbitals within the eigenstates as shown in (a). The comparison with the bands from hybrid functional (HSE06) calculation including SOC is shown in (b). Total and projected partial density of states are shown in (c). The edge states along lattice constant $a$ is shown in (d).

W atoms. It is noticeable that there are two W atoms in one unit cell. As shown in Fig. 3, the above selected $d$ atomic orbitals form bonding and anti-bonding states. The bonding and anti-bonding states of $d_{z^2}$ orbitals are even ($A_{1g}$) and odd ($A_{2u}$), respectively. Similarly, those from $d_{x^2-y^2}+d_{xy}$ are even ($E_g$) and odd ($E_u$) but having double degeneracy. The band inversion happens between the double degenerate $E_g$ and non-degenerate $A_{2u}$ states, which brings the nontrivial topology of bands. When the banding effect is considered from $\Gamma$ to $M$, the double degenerate $E_g$ states are split and there is no other band inversion happens. Further, the SOC introduces the spin degree of freedom and it opens a gap around Fermi level as shown in Fig. 4. Due to the heavy W element, the band gap is found to be as large
FIG. 3: (Color online) The band inversion mechanism in W$_2$CO$_2$. (a) W 5$d$ orbitals are split (b) under C$_{3v}$ crystal field (CF) with double degenerate $d_{x^2-y^2} + d_{xy}$ and single degenerate $d_{z^2}$ orbitals around Fermi level $E_F$. (c) The dimerization of two W atoms in each unit cell leads to bonding and anti-bonding states and band inversion between states with different parities (labeled by + and -). (d) The band dispersion along Γ-M does not induce other band inversion. (e) Including SOC opens band gap and introduces spin degeneracy in each band, with dashed and solid line representing opposite spin channels.

As 0.194 eV. Considering the possible underestimation of the band gaps within GGA, the hybrid functional (HSE06) calculation is used to check whether the above band inversion around Γ is robust. It is found that the band inversion is kept and the band gap is enhanced to as large as 0.472 eV. Such large band gap 2D TI has an advantage in observing quantum spin Hall effect at room-temperature or higher, which is appropriate for device applications.

For Mo$_2$CO$_2$ and Cr$_2$CO$_2$, both of them have the similar crystal structure as W$_2$CO$_2$ and are also dynamically stable as seen from the phonon spectra shown in Fig. 4. Since Mo and Cr have weaker SOC than W, they are expected to have narrower band gap than W$_2$CO$_2$. In fact, both of them show band structure of semimetals by having compensated electron and hole Fermi pockets. However, at each k point, one can still find well defined band gap with a curved Fermi level. The assumed occupied bands, as denoted with solid lines in Fig. 4, have the same $Z_2$ number as W$_2$CO$_2$. Therefore, both of them share the same band topology, as well as the underlying physics, with W$_2$CO$_2$.

Furthermore, we have investigated the correlation effect in d electrons of transition-metal M. For quite delocalized 5$d$ electrons in W and 4$d$ in Mo, detailed GGA+$U$ ($U$ is the...
FIG. 4: (Color online) The phonon spectrum (upper panel) and band structure with SOC (lower panel) for optimized stable Mo$_2$CO$_2$ (left panel) and Cr$_2$CO$_2$ (right panel). The assumed occupied (unoccupied) bands are denoted with solid (dashed) lines.

parameter for onsite Coulomb interaction) calculations ($U < 4.0$ eV) show that the correlation effect is negligible and the ground state of W$_2$CO$_2$ and M$_2$CO$_2$ are always nonmagnetic. The results discussed above are robust. However, for 3$d$ transition-metal Cr, simple GGA+$U$ ($U > 2.0$ eV) calculation for BB configuration gives out solution with magnetic properties. The above non-spin polarization calculations for Cr$_2$CO$_2$ are helpful to understanding the band gap dependence on the atomic number in that column, but not realistic for Cr$_2$CO$_2$ itself. However, this gives us the spin degree of freedom in material design based on MXene, which is very crucial to seeking Chern insulators hosting quantum anomalous Hall effect. The detailed studies on the dependence of $U$ value and magnetic configurations are left for future work.
IV. CONCLUSIONS

Based on the first-principles calculations, we have predicted that a family of oxygen functionalized MXene M$_2$CO$_2$ (M=W, Mo and Cr) are 2D TIs. The representative W$_2$CO$_2$ has robust band inversion, nontrivial $Z_2$ invariant and large band gap of 0.194 (0.472) eV within GGA (HSE06). It might satisfy all the four criteria of a "good" 2D TI. (1) easier production process by selective chemical etching method; (2) hosting QSHE at ambient condition; (3) high stability and antioxidant upon exposure to air; and (4) low production cost and consisting of environmental friendly elements.

Inspired by these findings, one can naturally think about obtaining more 2D TI candidates in other functionalized MXenes. The large number of MAX (more than 60$^{53,67}$ brings many possibilities of MXene$^{50}$ and huge space in finding topologically nontrivial materials. The possible changes would include replacing O$^2-$ with F$^-$ or (OH)$^-^{55,56,68}$ varying transition-metal M, replacing C with N or B$^{67}$ tuning the number of layers $n$ in MXene M$_{n+1}$C$_n$, etc. The material design or property tailoring with a single or any combination of the above changes will lead to more and better 2D TIs or Chern Insulators.

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