Thickness-dependent superconductivity and quantum spin Hall effects in $Ti_{n+1}O_n$ (n = 2, 3) MOenes

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MXene-like MOenes have shown intriguing properties, such as superconductivity in Ti₂O monolayers, direct band gaps, exotic quantum phase transitions, and strong light harvesting in Ti₂OX₂ (X = F, Cl) monolayers. However, stoichiometry engineering as a commonly tunable factor should be extended to study the thicknessdependent properties of MOenes. In this study, Ti_{n+1}O_n (n = 2, 3) MOenes and their functionalized counterparts are systematically investigated using *ab initio* calculations. Similar to the 2*H*-Ti₂O monolayer with a superconducting transition temperature T_c of 4.7 K, 2*H*-Ti₃O₂ and Ti₄O₃ monolayers are superconductors with a T_c of 4.4 and 3.7 K, respectively. More interestingly, 2*H*-Ti₃O₂F₂ and Ti₄O₃F₂ monolayers exhibit quantum spin Hall effects at room temperature with nontrivial gaps of 0.22 and 0.20 eV, respectively. The *d*-*d* band inversion mechanism is crucial for their topological nature. Therefore, the thickness-dependent features in Ti_{n+1}O_n MOenes will draw more attention to this emerging family of MOenes.

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I. INTRODUCTION

Since the Ti₃C₂ monolayer was first prepared by exfoliation of Ti_3AlC_2 in hydrofluoric acid at room temperature [1], two-dimensional (2D) transition metal carbides, nitrides, and carbonitrides (referred to as MXenes) have attracted tremendous attention. The formula for MXenes is $M_{n+1}X_nT_x$, where *M* is an early transition metal, *X* is either carbon or nitrogen, T_x represents surface termination units (such as hydrogen, hydroxyl, oxygen, or fluorine) based on practical synthesis environments, and n = 1-3 [1-3]. As expected, stoichiometry is a crucial factor for creating fabulous variations in the MXenes family, apart from the abundance of early transition metals, surface functional groups, and solid solutions. For example, 2D Ti₂C and Ti₂N are almost half-metallic ferromagnets, while single-layer (SL) Ti₃C₂ and Ti₃N₂ are antiferromagnets [4]. The Ti_2CF_2 monolayer exhibits multiple Dirac cones and giant spin-orbit splitting [5], despite the remarkably narrow band gap in SL Ti₃C₂F₂ [6]. Moreover, antiferromagnetic Ti₂NF₂ is a normal metal, whereas SL Ti₃N₂F₂ is a 2D topological insulator [7]. Of course, there are still many cases that show distinct features in the MXenes family, taking into account their atomic thickness [8]. Therefore, stoichiometry engineering is an indispensable technique for building 2D materials with unique properties.

Prior to this study, we proposed 2D transition metal oxide Ti_2O MOenes [9,10], which greatly extend the traditional

MXenes to 2D transition metal oxides. Similar to MXenes, the general formula for MXene-like MOenes is $M_{n+1}O_nT_x$, where O is the oxygen group element, such as O, S, Se, and Te. As reported, 2H- and 1T-Ti₂O MOenes are intrinsic superconductors. More intriguingly, surface halogenation in Ti_2OX_2 (X = F, Cl) monolayers leads to a direct band gap, together with long carrier lifetime and strong light-harvesting ability [10] and high thermoelectric performance [11]. In addition, Janus Ti2OFCl monolayers also exhibit direct semiconducting properties, quantum phase transitions, and weakened exciton binding strength [12]. More recently, the oxygen-terminated V₂O MOenes were reported as a promising electrocatalyst for the hydrogen evolution reaction [13]. MOenes and their Janus structures are reported to be important members of 2D piezoelectric materials [14]. Fortunately, 1T-Ti₂O films [15] and particles [16] were obtained via molten salt electrochemical synthesis and pulsed laser deposition, respectively. In this regard, 1T-Ti₂O and 2H-Ti₂O monolayers could be obtained with further effort. Recently, the existence of oxycarbide MXenes was directly confirmed by ultralow-energy secondary-ion mass spectrometry [17], which strongly supports the feasibility of this emerging MOene family. Here, the Ti₃C₂ T_x MXene shows up to ~30% oxygen in the carbon layers (the approximate formula is $Ti_3C_{1,4}O_{0,6}T_x$), but this is not necessarily a limit, and the pure $Ti_3O_2T_x$ MOene can be considered an extreme of the oxycarbides [18]. All in all, Ti_2O MOenes have shown many fascinating properties, and thus, extending the simplest stoichiometric ratio (Ti:O = 2:1) is urgent.

Motivated by the above-mentioned experimental and theoretical achievements with MOenes, in this work, $Ti_{n+1}O_n$

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FIG. 1. Atomic geometries for (a) 2H-Ti₃O₂ and (b) 2H-Ti₄O₃ monolayers in top (top panel) and side (bottom panel) views. The black solid and blue dashed lines in (a) and (b) indicate the primitive cell and rectangular conventional cell, respectively. The two possible functionalization sites on either side of the surface are "O-top" (on the top of the O sites) and "Ti-hollow" (on the hollow site of the hexatomic ring of the Ti and O sites). Top and side views of (c) 2H-Ti₃O₂F₂ and (d) 2H-Ti₄O₃F₂ monolayers.

and $Ti_{n+1}O_nT_2$ (n = 2, 3) MOenes are fully scrutinized with first-principles calculations. First, their stabilities are investigated, including their dynamical, mechanical, and thermal stabilities. Phonon spectra confirm the dynamical stability of 2H-Ti_{n+1}O_n and Ti_{n+1}O_n T_2 (n = 2, 3; T = F, H, and OH) monolayers, but the 1T phase and its functionalized phases are all dynamically unstable. Compared to the 2H-Ti₂O superconductor with a superconducting transition temperature T_c of 4.7 K, 2*H*-Ti₃O₂ ($T_c = 4.4$ K) and 2*H*-Ti₄O₃ ($T_c = 3.7$ K) show a slightly weakened superconductivity with increasing atomic thickness. However, surface functionalization strongly reduces the electron states near the Fermi level and hardens the phonon modes, thus greatly destroying their original superconductivity. In particular, fluorinated 2*H*-Ti_{*n*+1}O_{*n*} (n =2, 3) monolayers, namely, 2H-Ti_{n+1}O_nF₂ monolayers, show high stability and exhibit quantum spin Hall effects along with a nontrivial gap of 0.22 or 0.20 eV at the Heyd-Scuseria-Ernzerhof hybrid density functional (HSE06). The d-d band inversion process contributes to their topological nature. Our work stimulates the quantum spin Hall effects via stoichiometry engineering, enriching the exotic features of Ti-based MOenes.

II. COMPUTATIONAL METHODS

First-principles calculations were performed using the Vienna Ab initio Simulation Package (VASP) [19,20]. The Perdew-Burke-Ernzerhof functional was used to describe the exchange-correlation potentials within the generalized gradient approximation [21,22]. A cutoff energy of 500 eV for the plane-wave expansion and a *k*-point mesh of $25 \times 25 \times 1$ for the sampling grid were adopted in the calculations. A vacuum space of 15 Å between the layers was considered to minimize the neighbor interactions along the *z* vacuum direction. In the framework of density functional perturba-

tion theory, the phonon properties were explored with a $4 \times 4 \times 1$ supercell using the PHONOPY code [23]. The *ab initio* molecular dynamics (AIMD) simulations within a $4 \times 4 \times 1$ supercell were performed within the Nosé-Hoover thermostat [24]. HSE06 mixed with 25% exact Hartree-Fock exchange was also used to correct the band gap value. In order to study the topological properties, the Wannier charge center (WCC) and edge states were obtained using WANNIERTOOLS codes [25]. The tight-binding Hamiltonians with the maximally localized Wannier functions were constructed from Ti 3*d* orbitals and O 2*p* orbitals. In addition, the VASP-KIT code [26] was used for the postprocessing of the VASP simulations.

The electron-phonon coupling (EPC) was studied using the QUANTUM ESPRESSO software [27,28]. The calculations were performed using the optimized norm-conserving Vanderbilt pseudopotentials [29], with the plane-wave kinetic-energy cutoff and the charge-density cutoff set to 80 and 320 Ry, respectively. A **k**-point mesh of $36 \times 36 \times 1$ with a Methfessel-Paxton smearing width of 0.02 Ry and a **q** mesh of $6 \times 6 \times 1$ for dynamic and EPC matrix elements were treated. According to the BCS microscopic theory [30], the Migdal-Eliashberg equations were adopted to study the superconductivity [31]. More detailed methods are given in the Supplemental Material (SM) [32] (see also Ref. [33] therein).

III. RESULTS AND DISCUSSION

A. Crystal structures of 2H-Ti_{*n*+1}O_{*n*} monolayers

The atomic structures of SL 2H-Ti_{n+1}O_n and 1T-Ti_{n+1}O_n (n = 2, 3) are shown in Fig. 1 and Fig. S1 in the SM [32], respectively. In the following, n equals 2 and 3 unless otherwise stated. First, 2H-Ti_{n+1}O_n monolayers are found to be dynamically stable, whereas 1T phase monolayers are kinetically unstable, with apparent imaginary frequencies in the

Brillouin zone (BZ; see the SM, Fig. S2) [32]. We therefore focus only on the 2H phases. There are two inequivalent types of Ti atoms: the inner Ti atomic layers (bonded to O atoms) and the outer Ti atomic layers (exposed to the environment). 2H-Ti_{*n*+1}O_{*n*} monolayers crystallize in a hexagonal structure, with each inner Ti atom hexahedrally coordinated with the neighboring O atoms, and have a space group of $P\bar{6}m2$ (No. 187). To determine the ground states of SL 2H-Ti₃O₂ and Ti_4O_3 , possible nonmagnetic (NM), ferromagnetic (FM), and antiferromagnetic (AFM) spin configurations are considered within their conventional cells (see the SM, Figs. S3 and S4) [32]. As listed in Tables S1 and S2 in the SM [32], different from SL 2H-Ti₂O [10], 2H-Ti₃O₂ is a FM spin configuration with a magnetic moment of $0.87\mu_B$ per outer Ti atom [see the SM, Fig. S3(a)] [32]. Meanwhile, 2H-Ti₄O₃ behaves as a FM state with the lowest total energy [see the SM, Fig. S4(a)] [32]; the magnetic moment per outer dangling Ti atom is $0.85\mu_{B}$. Clearly, the ground states of $Ti_{n+1}O_n$ (n = 1-3) are strongly dependent on the atomic thickness, analogous to $Ti_{n+1}C_n$ and $Ti_{n+1}N_n$ (n = 1, 2) MXenes [4]. The lattice constants of 2*H*-Ti₃O₂ are optimized to be a = 2.95 Å and b = 4.70 Å, comparable to those of 2H-Ti₄O₃ (a = 2.91 Å, b = 4.77Å). The electron localization function (ELF) plots (see the SM, Fig. S5) [32] show the Ti-O bonds in the 2H-Ti₃O₂ and 2H-Ti₄O₃ monolayers are ionic, with bond lengths of 2.26 and 2.25 Å, respectively, slightly larger than that in SL 2H-Ti₂O (2.15 Å). More interestingly, some anionic electrons are distributed on the surfaces of the outer Ti atoms due to the dangling Ti 3d orbitals, as previously observed in Ti_2O MOenes [9,10], favoring ultrafast ion transport and strong ion adsorption on the surfaces.

The evaluated melting temperatures of SL 2H-Ti₃O₂ and 2H-Ti₄O₃ are both around 600–900 K (see the SM, Fig. S6) [32], comparable to that of SL 2*H*-Ti₂O [10], reflecting the robustness of the thermal stability to the increase in layer thickness for SL 2*H*-Ti_{*n*+1}O_{*n*} (n = 1-3). The calculated elastic constants C_{ii} ensure mechanical stability (see the SM, Table S3), according to the Born elastic criteria for the rectangular structure, namely, $C_{11} > 0$, $C_{66} > 0$, and $C_{11}C_{22} - C_{66} > 0$ $C_{12}^2 > 0$ [34]. Here, Young's modulus Y quantifies the inplane stiffness [35,36] since the thickness is ambiguous in 2D materials. The calculated Y along the x and y directions are 128.4 and 127.65, 120.95 and 294.95, and 318.05 and 294.61 N/m for SL 2H-Ti₂O, Ti₃O₂, and Ti₄O₃, respectively. It is clear that the in-plane stiffness values of 2H-Ti_{n+1}O_n (n =1–3) monolayers increase with increasing atomic thickness. What is more, the in-plane stiffness values of SL 2*H*-Ti_{*n*+1}O_{*n*} are smaller than or comparable to those of SL MoS_2 (140 N/m) [37], B₂O (130 N/m) [38], h-BN (258 N/m) [39], and graphene (340 N/m) [40], reflecting their soft properties and feasible strain engineering. In addition, Poisson's ratio v, which describes the mechanical response of the 2*H*-Ti_{*n*+1}O_{*n*} monolayers to uniaxial strain, reveals anisotropic mechanical response.

B. Metallicity and superconductivity in SL 2H-Ti_{*n*+1}O_{*n*}

2H-Ti_{*n*+1}O_{*n*} monolayers display metallic features, as indicated by their projected band structures in Fig. 2. For FM SL 2H-Ti₃O₂, there are two spin-up bands crossing the Fermi

level along the Γ -Y path [Fig. 2(a)], and three spin-down bands cross the Fermi level [Fig. 2(b)], which are mainly contributed by Ti $d_{x^2-y^2,xy}$. Slightly different in SL FM 2*H*-Ti₄O₃, the spin-up electronic states lead to two band crossings of the Fermi level along the Γ -Y path, which originate mainly from the Ti $d_{x^2-y^2,xy}$ orbitals with a small amount from Ti d_{z^2} orbitals [Fig. 2(d)]. In addition, two spin-down bands dominated by the Ti $d_{x^2-y^2,xy}$ orbitals contribute its metallic states along the Γ -X path [Fig. 2(e)]. In order to understand the impact of magnetism, projected band structures for NM 2H-Ti₃O₂ and Ti_4O_3 are also presented in Figs. 2(c) and 2(f), respectively. Clearly, when compared with the band structures of NM 2H- $Ti_{n+1}O_n$, the spin-up (spin-down) band structures move down (up) about 0.35 eV. All in all, rich metallic features could imply underlying superconductivity in SL 2*H*-Ti_{n+1}O_n, as reported in bulk Ti-O systems [41-43] and Ti₂O monolayers [9,10]. As listed in Tables S1 and S2, the energy differences between the different magnetic configurations are nearly degenerate. Therefore, long-range magnetic ordering is unlikely to be stable in 2H-Ti_{*n*+1}O_{*n*}. In this regard, we choose the NM ground states when studying their superconductivity [44,45]. In addition, dominant pairing mechanisms in superconducting systems with magnetic states are actively being debated. In general, antiferromagnetic fluctuations [46,47], EPC [48–50], and the cooperative effect of the two [48] are frequently explored. Moreover, the EPC plays a crucial role in enhancing T_c among magnetic systems [48–50]. Therefore, the potential superconductivity in NM 2*H*-Ti_{n+1}O_n monolayers is investigated below in the framework of BCS microscopic theory [30].

As depicted in Figs. 3(a) and 3(d), due to the significant atomic mass difference between Ti and O atoms, the phonon modes are completely separated, resulting in optical phonon gaps of ~3, 1, and 0.3 THz for SL 2*H*-Ti₂O, 2*H*-Ti₃O₂, and 2*H*-Ti₄O₃ at the Γ point, respectively. Clearly, these optical phonon gaps decrease simultaneously with the increase in crystal thickness. Additionally, the vibrations of Ti atoms are significantly responsible for the frequency region below 11 THz, including three acoustic branches formed by the out-of-plane (ZA), in-plane transverse (TA), and in-plane longitudinal (LA) modes. Intriguingly, the apparent Kohn anomalies are located at the *M* point of the ZA and LA modes, which is a good factor to induce substantial EPC in this region [38,51–53]. Meanwhile, a higher-frequency region (>11 THz) is occupied by the lighter O atoms.

The phonon branches weighted by EPC λ_{qv} can distinguish the contribution of each branch to the total EPC constant λ . As shown in Figs. 3(b) and 3(e), the main origins of superconductivity in SL 2*H*-Ti₃O₂ and Ti₄O₃ are largely generated below the 4 THz region. As a result, the Eliashberg spectral functions $\alpha^2 F(\omega)$ exhibit two major peaks in this low-frequency region, causing a large increase in the cumulative $\lambda(\omega)$: about 48.2% (54.5%) of the total EPC for SL 2*H*-Ti₃O₂ (Ti₄O₃). This is due to the fact that the apparent Kohn anomalies exist in the ZA and LA modes at the *M* point, where the in-plane vibrations of the Ti atoms (Ti *xy*) are mostly dominant. Meanwhile, two relatively smaller Kohn anomalies located at the *K* points in the first two optical branches also lead to a further increase in $\lambda(\omega)$, where the out-of-plane vibrations of Ti (Ti *z*) mainly contribute. In addition, the midfrequency region (4–8 THz)



FIG. 2. The projected (a) and (b) spin-up and (d) and (e) spin-down band structures for the FM 2H-Ti₃O₂ and 2H-Ti₄O₃ monolayers. For comparison, projected band structures of NM SL 2H-Ti₃O₂ and 2H-Ti₄O₃ are depicted in (c) and (f), respectively.

leads to a 42.8% and 41.8% enhancement of the total EPC for 2H-Ti₃O₂ and Ti₄O₃ monolayers, respectively. Furthermore, the maps of the EPC distribution in the BZ also show that the largest EPC originates from the M point and the relatively small EPC is located around the K point [Figs. 3(c) and 3(f)]. This is because electrons and phonons typically generate effective couplings in these Kohn anomalies [38,51–53]. Using the simplified McMillan-Allen-Dynes formula [31], T_c of SL 2H-Ti₃O₂ and Ti₄O₃ are estimated to be 4.4 and 3.7 K, respectively. These T_c values are higher than those of Ti₂C (1.3 K) [54], Ta₂N (2.1 K) [55], Mo₂CT₂ (T = 0, S, Se; 0.1-1.4 K) [56], Nb₂CSe₂ (0.53 K), and Nb₂CTe₂ (0.27 K) [57] and comparable to those of Mo_2C (3.0 K) [54,58], W_2C (4.2 K), Sc₂C (4.1 K) [55], Nb₂CS₂ (4.5 K) [57], and Nb₂CCl₂ (5.2 K) [59] in theories and functionalized Nb₂C (4.5–7.1 K) [60] and Mo₂C (2.5–4.9 K) [61] MXenes in experiments. In addition, the sensitivity of the effective screened Coulomb repulsion constant μ^* to T_c was further investigated by varying μ^* from 0.08 to 0.15 [38]. As expected, the T_c values in 2H- $Ti_{n+1}O_n$ (n = 1-3) monolayers decrease monotonically with increasing μ^* (see the SM, Fig. S7).

As discussed above, the superconductivity of SL 2*H*-Ti_{*n*+1}O_{*n*} (n = 1-3) is mainly due to the coupling between Ti 3*d* electrons and Ti atom vibrations. As shown in Table I, T_c of 2*H*-Ti_{*n*+1}O_{*n*} monolayers decrease slightly with increasing thickness. This is attributed to the fact that the density of states at the Fermi level $N(E_F)$ originates mainly from the outer sur-

face of the Ti atoms (see the SM, Fig. S8) [32], and thus, the differences between $N(E_F)$ are negligible. More cautiously, compared to those in SL 2H-Ti₄O₃, the Kohn anomalies in SL 2H-Ti₃O₂ with slightly softer modes lead to a slightly larger λ and hence a slightly larger T_c [Fig. 3(b)]. When compared with those of 2H-Ti₂O, the logarithmic average frequency ω_{log} values of 2H-Ti₃O₂ and Ti₄O₃ are smaller to some extent due to the thickness effects. Although λ for 2*H*- Ti_2O is relatively smaller, its T_c is slightly higher [Eq. (S5) in the SM]. In this respect, the EPC in 2H-Ti_{n+1}O_n monolayers may be slightly reduced along increasing atomic thickness but is retained in the strong Ti-O interactions, similar to the 2D W₂N₃ superconductor [52]. In addition, fascinating Weyl fermions actually exist in NM 2H-Ti₃O₂ and Ti₄O₃ monolayers (see the SM, Fig. S8) [32], located at the Γ point and about 0.5 eV above the Fermi level. To obtain the Weyl fermions near the Fermi level, surface functionalization is an efficient way to tune the Fermi level [35]. We will discuss this later.

C. Surface functionalizations for SL 2H-Ti_{n+1}O_n

2H-Ti_{*n*+1}O_{*n*} MOenes are basically terminated by unsaturated Ti atoms and thus are susceptible to termination by surface functionalizations, i.e., fluoridation, hydrogenation, oxidation, and hydroxylation. The two main possible termination sites (denoted "T"), denoted "O-top" and "Ti-hollow,"



FIG. 3. Phonon spectra of SL (a) 2*H*-Ti₃O₂ and (d) Ti₄O₃, resolved with respect to the Ti and O atomic vibrations. Phonon dispersions for (b) 2*H*-Ti₃O₂ and (d) Ti₄O₃ monolayers are marked with a color bar proportional to the partial EPC strength λ_{qv} (left panel), together with the Eliashberg spectral functions $\alpha^2 F(\omega)$ and the cumulative frequency-dependent EPC function $\lambda(\omega)$ (right panel). The red circle marks the Kohn anomaly point. (c) and (f) The EPC λ_{qv} distributions in the BZ for SL 2*H*-Ti₃O₂ and Ti₄O₃, respectively.

are considered in Fig. 1. Similar to 2*H*-Ti₂O MOenes [9,10], the most stable sites for fluoridation and hydroxylation groups are above the Ti-hollow, whereas hydrogenation and oxidation groups are above the O-top. As a result, these surface terminations saturate the dangling Ti 3*d* orbitals, leading to their NM ground states. Based on the most energetically stable crystals, 2*H*-Ti_{*n*+1}O_{*n*}T₂ (*T* = F, H, and OH) monolayers have been shown to be kinetically stable, with the exception of SL 2*H*-Ti_{*n*+1}O_{*n*}O₂ (see the SM, Figs. S9 and S10) [32]. Unfortunately, 1*T*-Ti_{*n*+1}O_{*n*</sup>T₂ (*T* = F, H, O, and OH) monolayers are}

TABLE I. Superconductive parameters $N(E_F)$ (in units of states per spin per rydberg per cell), ω_{\log} , λ , and T_c .

Compound	$N(E_F)$	ω_{\log} (K)	λ	$T_c(\mathbf{K})$
SL 2H-Ti ₂ O	38.02	246.96	0.56	4.7 [10]
$SL 2H-Ti_3O_2$	30.73	213.52	0.58	4.4
SL $2H$ -Ti ₃ O ₂ F ₂	1.42	408.61	0.02	0
SL 2H-Ti ₃ O ₂ H ₂	13.84	434.42	0.24	0.01
SL $2H$ -Ti ₃ O ₂ (OH) ₂	16.05	573.73	0.27	0.09
SL 2H-Ti ₄ O ₃	34.48	212.72	0.55	3.7
SL 2H-Ti ₄ O ₃ F ₂	1.95	420.32	0.02	0
SL 2H-Ti ₄ O ₃ H ₂	20.37	452.19	0.24	0.02
SL 2H-Ti ₄ O ₃ (OH) ₂	18.85	566.04	0.26	0.02

still dynamically unstable in their freestanding structure (see the SM, Fig. S11) [32]. As given in Table S4, 2H-Ti_{n+1}O_n T_2 (T = F, H, and OH) monolayers also fulfill the mechanical stability criteria for hexagonal crystals: $C_{11} > |C_{12}|$ and $C_{66} >$ 0 [34]. Furthermore, their in-plane stiffness values increase with increasing thickness. The equal ν values along the x and y directions mean they have isotropic mechanical properties. More intriguingly, the Fermi level in NM 2H-Ti_{n+1}O_nT₂ monolayers is, indeed, modulated to different degrees, which is strongly related to the functional groups. 2H-Ti_{n+1}O_nT₂ (T = F, H, and OH) monolayers show semimetallic features originating from the Ti 3d orbitals (Figs. S9 and S10). Meanwhile, the intrinsic superconductivity in SL 2*H*-Ti_{*n*+1}O_{*n*} is destroyed by surface functionalizations due to the huge decrease in $N(E_F)$ (Table 1) and the hardened phonon features. On the other hand, upon surface fluoridation in SL 2H-Ti₃O₂ and Ti₄O₃, charming Weyl fermions are purely located at the Fermi level [see the SM, Figs. S9(e) and S10(e)] [32]. Therefore, we will focus our attention on 2H-Ti_{n+1}O_nF₂ (n = 2, 3) monolayers.

D. The quantum spin Hall effects in SL 2H-Ti_{*n*+1}O_{*n*}F₂

Now we turn to the 2H-Ti₃O₂F₂ and Ti₄O₃F₂ monolayers, as explicitly shown in Figs. 1(c) and 1(d), respectively. They



FIG. 4. Projected band structures for (a) and (b) $2H-Ti_3O_2F_2$ and (c) and (d) $Ti_4O_3F_2$ monolayers calculated (a) and (c) without and (b) and (d) with SOC effects. Edge state plots for SL (c) $2H-Ti_3O_2F_2$ and (f) $Ti_4O_3F_2$. The Fermi level is at 0 eV.

also crystallize in a hexagonal structure with space group $P\bar{6}m2$, and the lattice constants of 2H-Ti₃O₂ and Ti₄O₃F₂ monolayers are a = b = 2.83 and 2.82 Å, respectively. Moreover, the Ti-F bonds with a bond length of 2.08 Å show strong ionic bonding interactions, as studied with the ELF (see the SM, Fig. S12) [32]. Meanwhile, the Ti-O bonds in 2H-Ti₃O₂F₂ and Ti₄O₃F₂ monolayers are both optimized to 2.16 Å, which is about 0.1 Å smaller than their freestanding phases. On the other hand, the surface fluoridation leads to a higher thermal stability in SL 2H-Ti_{n+1}O_nF₂, reaching more than 1500 K (see the SM, Fig. S13) [32].

When spin-orbit coupling (SOC) is not considered, the valence band maximum (VBM) and conduction band minimum (CBM) touch quadratically at the Γ point of the Fermi level, forming a two-component 2D double Weyl fermion with an E' irreducible representation of the D_{3h} point group [Figs. 4(a) and 4(d)]. The Fermi level must cut directly through the E' states because of the band filling. Thus, SL 2H-Ti₃O₂F₂ and Ti₄O₃F₂ maintain a semimetal phase with a single Fermi point as long as the threefold rotational symmetry is preserved. These degenerate touching states are mainly occupied by Ti $d_{x^2-y^2,xy}$ orbitals. On the other hand, when SOC is considered, these degenerate Weyl fermions are split in SL 2H-Ti₃O₂F₂ [Fig. 4(b)] and $Ti_4O_3F_2$ [Fig. 4(e)], giving SOC gaps of 32 and 29 meV, respectively. Although the direct band gaps are shown at the Γ point, the VBM is located above the Fermi level and also leads to semimetal properties. According to the orbital composition analysis, the SOC does not generate any band inversion, which is a key factor in band topology. What is more, these orbitals near the Fermi level for SL 2*H*-Ti_{*n*+1}O_{*n*}F₂ come from the inner Ti atoms (see the SM, Fig. S8) [32], which are fully bonded to O atoms, rather than the outer Ti atoms bonded to F atoms in the Ti₂OF₂ monolayer. Thus, these electronic structures are very different from the semiconducting SL Ti₂OF₂ and yield exotic electronic structures in the Ti-based MOene family. In order to obtain an effective model describing the low-energy fermions for the Γ point without SOC, we construct an effective model based on the *E'* states as the basis. Subjected to time-reversal symmetry and *D*_{3*h*} symmetry operations, which include twofold rotation *C*₂, threefold rotation *C*₃, sixfold rotoreflection *S*₆, and mirror *M*, the *kp* Hamiltonian expanded up to *k*th quadratic order has the general form

$$H(k) = [c_0 + c_1(k_x^2 + k_y^2)]\sigma_0 + 2c_2k_xk_y\sigma_1 + c_2(-k_x^2 + k_y^2)\sigma_3, \qquad (1)$$

where c_i (i = 0, 1, 2) are band parameters extracted by fitting band structures. σ_i (i = 0, 1, 3) are Pauli matrices. Exactly at the Γ point (k = 0), it can be seen that c_0 are the energies of the E' states. By determining the band parameters of this general Hamiltonian, we can quantitatively understand the pronounced changes in the low-energy band structures at the Γ point.

Moreover, we also construct the effective model for the Γ point with SOC; the obtained Hamiltonian expanded up to *k*th



FIG. 5. (a)–(d) Band structure evolutions of SL 2*H*-Ti₃O₂F₂ under biaxial strain without SOC. The Fermi level is set to 0 eV. (e) Schematic evolution of the electronic bands at the Γ points as the lattice constant is uniformly increased. The corresponding band irreducible representations at the Γ point are also marked. a_0 and E_f indicate the optimized lattice constant and Fermi level, respectively.

quadratic order has the general form

$$H(k) = \left[c_0 + c_1 \left(k_x^2 + k_y^2\right)\right] \sigma_0.$$
 (2)

It is clear that with SOC, there are twofold Kramers degenerate states at the Γ point.

Since 2H-Ti_{*n*+1}O_{*n*}F₂ monolayers lack inversion symmetry, the Z_2 invariant values are determined to be 1 via WCC studies (see the SM, Fig. S14) [32], where an arbitrary line crosses the WCC from left to right an odd number of times. Simultaneously, the nontrivial edge states connect the bulk valence and conduction bands to form a Dirac-cone-like dispersion along the Γ -K path, as shown in Figs. 4(c) and 4(f). The electrons in such edge states have opposite velocities in opposite spin channels, giving rise to forbidden backscattering as long as the time-reversal symmetry is preserved [7]. Therefore, SL 2*H*-Ti₃O₂F₂ and Ti₄O₃F₂ are 2D topological insulators, which favor band inversion occurring before the introduction of the SOC. We will explain this later. The HSE06 calculations correct these nontrivial gaps to 0.22 and 0.20 eV, which are larger than or comparable to those in the Ti₃N₂F₂ (0.05 eV) [7], Mo₂TiC₂O₂ (0.17 eV) [62], Mo₂MC₂O₂ (M= Ti, Zr, Hf; (0.10-0.20 eV)[63], W_2CO_2 (0.47 eV) [64], $M'_2 M'' C_2 O_2$ (M' = Mo, W; M'' = Ti, Zr, Hf; 0.12-0.41 eV) [65], and $M'_2M''C_2F_2$ (M' = V, Nb, or Ta; M'' = Ti, Zr, or Hf; 0.034–0.32 eV) [66] MXenes using the HSE06 hybrid functional calculations. In this context, they are totally sufficient for practical applications at room temperature. Moreover, the topological properties of 2H-Ti_{n+1}O_nF₂ monolayers may be insensitive to the substrate effects since their nontrivial topological features originate from the Ti atoms located inside the crystals, rather than on the surfaces [63,66,67].

To understand the band inversion process in more detail, taking SL 2*H*-Ti₃O₂F₂ as an illustration, the evolution of its band structures is plotted in Fig. 5. Within the point symmetry of the crystal lattice, the Ti 3*d* orbitals can be split into d_{xz} , d_{yz} , $d_{x^2-y^2}$, d_{xy} , and d_{z^2} . Here, we consider only the Ti $d_{x^2-y^2}$, Ti d_{xy} , and Ti d_{z^2} orbitals, which are dominant around the Fermi level. As shown in Figs. 5(a) and 5(b), when the lattice is compressed more than ~5% and SOC is absent, the band gaps open, and the band characters of the CBM change qualitatively, with this band contributed by Ti d_{z^2} , while the two degenerate VBMs are composed of Ti $d_{x^2-y^2,xy}$ orbitals. At this time, the 2H-Ti₃O₂F₂ monolayer is a trivial band insulator, as the band irreducible representations for the VBM and the degenerate CBM are A' and E', respectively. As the lattice is gradually stretched, the hybridization between neighboring d orbitals decreases. As a result, the doubly degenerate Ti $d_{x^2-v^2,xy}$ orbitals shift down in energy, while the Ti d_{z^2} orbitals move above the Fermi level. Meanwhile, these two states have different band irreducible representations, and this is exactly how band inversion occurs. Once the band inversion occurs, the system remains semimetallic because the Fermi energy is exactly in the doubly degenerate Ti $d_{x^2-y^2,xy}$ states. However, the SOC removes this double degeneracy, and the system becomes a nontrivial insulator. In this process, SOC induces only a finite band gap but no band inversion. Similar d-dband inversion was also found in the $Ti_3N_2F_2$ [7], $Mo_2MC_2O_2$ (M = Ti, Zr, Hf) [63], $M_2 \text{CO}_2$ (M = Mo, W, Cr) [64], $M'_2M''C_2O_2$ (M' = Mo, W; M' = Ti, Zr, Hf), and $M'_2M''_2C_3O_2$ (M' = Mo, W, M'' = Ti, Zr) MXenes [65] and ZrTe₅ monolayers [68]. Note that the 2H-Ti₄O₃F₂ monolayer has a crystal symmetry similar to that of SL 2*H*-Ti₃O₂F₂ discussed above. Therefore, SL 2H-Ti₄O₃F₂ has the same band topology, as well as the underlying physics.

IV. CONCLUSIONS

In conclusion, SL $Ti_{n+1}O_n$ (n = 2, 3) MOenes and their surface functionalizations were fully studied from the atomic crystal, stability, electronic, superconducting, and topological aspects. However, only SL 2*H*-Ti_{*n*+1}O_{*n*} and Ti_{*n*+1}O_{*n*}T₂ (T = F, H, and OH) remain dynamically stable with increasing atomic thickness. 2*H*-Ti₃O₂ and Ti₄O₃ monolayers are 2D superconductors with T_c of 4.3 and 3.7 K, respectively. Unfortunately, 2*H*-Ti_{*n*+1}O_{*n*}T₂ monolayers exhibit nonsuperconducting traits, with reduced electrons near the Fermi level and hardened phonon modes. In addition, 2*H*-Ti_{*n*+1}O_{*n*}F₂ monolayers possess higher stability and are topological insulators, broadening the range of topologically nontrivial materials. The *d*-*d* band inversion is a crucial factor for producing band topology. Furthermore, *kp* effective models help to describe these low-energy bands. Our work revealed the thickness-dependent features of Ti-based MOenes via stoichiometry engineering and should lead to more interest in MOenes materials.

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