Topological nodal lines in bulk and monolayer $\text{W}_2\text{O}_3\text{I}_4$

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By means of first-principles calculations, we study the topological nontrivial electronic structures and lattice dynamics of bulk and monolayer $\text{W}_2\text{O}_3\text{I}_4$. We find that both of them are nodal-line semimetals in the absence of spin-orbit coupling (SOC), in which the nodal lines are induced by the band inversion between conduction and valence bands contributed by $\text{W}d$ and $\text{I}p$ orbitals. Moreover, $\text{W}_2\text{O}_3\text{I}_4$ bulk and monolayer exhibit excellent mechanical and thermal stability. By studying the external field modulation of topological nodal lines without SOC effect in monolayer $\text{W}_2\text{O}_3\text{I}_4$, we find that the nodal lines are extremely robust against the biaxial strain but destroyed under vertical electric field due to the breaking of horizontal mirror symmetry. It is studied that the SOC effect here is large and non-negligible, and after considering the SOC effect, $\text{W}_2\text{O}_3\text{I}_4$ bulk and monolayer undergo change of topological state from a topological nodal-line semimetal to a topological insulator. Our work not only extends the member of inorganic three-dimensional and two-dimensional topological semimetals library but also provides a prototype material candidate to investigate the double nodal-line surface states.

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I. INTRODUCTION

Topological quantum materials including topological insulators and topological semimetals have been of great interest in the past decade for their intriguing physics from nontrivial electronic structures to transport properties [1–7]. The characteristic band crossing points with different degeneracy and dimensionality emerge between conduction and valence bands near the Fermi level in the Brillouin zone (BZ). The well-known topological Dirac and Weyl semimetals have band crossings with fourfold and twofold degeneracies at zero-dimensional (0D) nodal points, where the quasiparticle excitations are analogous to relativistic Dirac and Weyl fermions, respectively. Dirac and Weyl semimetals have been theoretically predicted [8–15] and experimentally confirmed [16–22], and the intriguing semimetal with coexisting Dirac-Weyl points was also proposed [9]. Beyond the Dirac and Weyl semimetals, a number of topological materials have been investigated extensively, such as nodal-line semimetals (NLS) [23], triple point semimetals [24,25], and double Dirac semimetals [26].

In 2011, Burkov et al. presented the concept of three-dimensional (3D) line-node semimetal with broken time-reversal symmetry [11] and after that the 3D NLS state was consequently extended to the cases of time-reversal invariant systems [27,28]. In recent years, a number of candidates of 2D and 3D NLS have been theoretically predicted by first-principles calculations [29–33]. At this stage, there are still few experimentally realized NLS in two and three dimensions [34], and it is an urgent task to explore and modulate their excellent topological properties.

Mixed anionic materials may contain a metal cation and two different anions, such as various 1D and 2D oxyhalides, nitrohalides, phosphorous dichalcogenides, and sili-tritellurides [35]. The tungsten oxyhalide properties were investigated in vapor phase [36]. Several members of the tungsten oxyhalide family including $\text{WOCl}_4$, $\text{WOBr}_4$, $\text{WO}_2\text{Br}_2$, and $\text{WO}_2\text{I}_2$ are comprised of 1D chains and 2D van der Waals layers. Low-dimensional systems of such tungsten oxyhalides may offer unique physical and chemical properties, such as the interesting noncollinear ferroelectricity [37] and quantum spin Hall effect [35], which have potential applications in optics [38], catalysis [38], sensors [38], quantum computing [38], and nanoelectronics [39].

Recently, a new phase of tungsten oxyhalide $\text{W}_2\text{O}_3\text{I}_4$ has been synthesized in experiment [40]. Surprisingly this material has never been studied by theoretical prediction, nor

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has its specific electronic structure been discussed. The experiment work reported two new structures of WO$_2$I$_2$ of Immm phase and W$_2$O$_3$I$_4$ of $I2/m$ phase. The $I2/m$ structure of W$_2$O$_3$I$_4$ is relatively more complex than that of Immm WO$_2$I$_2$, both of which are found to be layered materials. WO$_2$I$_2$ is composed of W-centered octahedra with solely corner sharing through oxygen atoms, but, in the case of W$_2$O$_3$I$_4$, edge sharing through iodine atoms is found [40]. As a van der Waals layered material, we can naturally associate it with an exploration of its two-dimensional nature.

In our present work, by means of first-principles calculations, we first demonstrate the stability of W$_2$O$_3$I$_4$ (bulk and its monolayer) from mechanical and thermal perspectives. Then we find that W$_2$O$_3$I$_4$ bulk and monolayer are Dirac NLS without the spin-orbit coupling (SOC) effect and are confirmed to be topological insulators in the presence of the SOC. Strain engineering, as an efficient strategy to test the robustness of topological electronic structures, shows that the nodal line is stable against the biaxial strains without SOC effect. Moreover, it is found that a moderate external electric field may destroy the nodal line. As a van der Waals material, the calculated cleavage energy of W$_2$O$_3$I$_4$ ($0.271$ $\text{J/m}^2$) is smaller than graphene, implying that monolayer W$_2$O$_3$I$_4$ is possible to exfoliate in experiment. Our results offer a realistic material platform for the exploration of the Dirac nodal-line semimetals.

II. RESULTS AND DISCUSSIONS

A. Crystal structures and stabilities of bulk and monolayer W$_2$O$_3$I$_4$

The crystal structure of bulk W$_2$O$_3$I$_4$ of space group $I2/m$ is shown in Fig. 1(a). It contains two distinct tungsten atoms with different network connectivity. The structure of monolayer W$_2$O$_3$I$_4$ is displayed in Fig. 1(b). For W$_1$ and W$_2$, the network is similar to the structure of WO$_2$I$_2$ (see Supplemental Material Fig. S1 [41]), which characterizes the two-dimensional corner connectivity of WO$_2$I$_2$ octahedra by shared oxygen atoms. As for W$_3$ and W$_4$, we can find edge-sharing WO$_2$I$_2$ octahedra connected via iodine atoms, accompanied by alternating short and long W-W distances. Obviously, two WO$_2$I$_2$ octahedra are different with different shared atoms: the W$_1$ octahedra can be marked as (WO$_4$/I$_2$) as there are two O atoms shared with the neighbor W$_1$ and the other two are shared with the neighbor W$_2$. It can be marked as (WO$_2$/I$_4$/2) for W$_2$ as there are two O atoms shared with the neighbor W$_1$ and four iodine atoms are shared with the neighbor W$_2$. The optimized lattice constants of bulk W$_2$O$_3$I$_4$ are $a = b = 8.450$ Å and $c = 9.323$ Å. The optimized W-O distances are 1.933 and 1.897 Å for W$_1$, and 1.868 Å for W$_2$. The optimized alternating short and long W-W distances for W$_2$ are 3.104 and 4.425 Å. The lattice parameters and bond lengths are in good agreement with the reported experiment data and are summarized in Supplemental Material Table S1 [41] and Fig. S2 [41].

Since the bulk W$_2$O$_3$I$_4$ is a van der Waals layered structure, one may expect to realize the monolayer W$_2$O$_3$I$_4$. So, we constructed a single-layer structure of W$_2$O$_3$I$_4$ and it has an orthorhombic lattice with space group Cnmm as shown in Fig. 1(b). The optimized lattice constants of monolayer W$_2$O$_3$I$_4$ are $a = b = 8.452$ Å. The optimized W-O bonds for monolayer W$_2$O$_3$I$_4$ are 1.933, 1.897, and 1.869 Å. The optimized alternating short and long W-W distances are 3.110 and 4.421 Å, respectively. The lattice parameters and bond lengths are summarized in Table S1 [41] and Fig. S3 [41]. To check whether it is possible to exfoliate W$_2$O$_3$I$_4$ monolayer in practice, the cleavage energy density is calculated as shown in Fig. 1(c) to be $0.271$ J/m$^2$ which is lower than graphene ($0.325$ J/m$^2$ theoretically [42] and $0.371$ J/m$^2$ [43] experimentally). We refer to $(d - d_0)/d_0$ to indicate the separation when the monolayer is peeled out from the parent material, where $d$ indicates the distance of the monolayer W$_2$O$_3$I$_4$ monolayer from its bulk, and $d_0$ denotes the normal layer-to-layer distance in the W$_2$O$_3$I$_4$ crystal. Thus, the exfoliation of a monolayer from bulk W$_2$O$_3$I$_4$ should be feasible in the experiment.

To demonstrate the dynamic and thermal stabilities of bulk and monolayer W$_2$O$_3$I$_4$, we perform the phonon spectra calculations and ab initio molecular dynamics (AIMD) simulations. As shown in Figs. S4(a) and S4(b) [41], there is no obvious imaginary mode in the whole Brillouin zone, indicating that the structures of monolayer and bulk W$_2$O$_3$I$_4$ are dynamically stable against distortion perturbations. The AIMD simulations of 3000 fs for monolayer and bulk W$_2$O$_3$I$_4$ at 300 K are shown

![FIG. 1. Top and side views of (a) bulk W$_2$O$_3$I$_4$ and (b) monolayer W$_2$O$_3$I$_4$. (c) The cleavage energy density of W$_2$O$_3$I$_4$.](image_url)
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FIG. 2. (a) The orbital-resolved band structures of bulk W2O3I4. (b) Top and side views of nodal lines in the whole BZ and its (100)/(010) surface. (c) The surface state near Fermi energy level of bulk W2O3I4 at the (100) surface. (d) The band structure of bulk W2O3I4 in the presence of SOC effect and zoom-in views of the gap opening of degenerate nodes.

We further derived the drumheadlike surface state near Fermi energy level of the (100) surface of bulk W2O3I4 shown in Fig. 2(c) as evidence of a topological nodal-line semimetal without considering SOC effect. We can see the surface state clearly and in the path along the Γ-X, M-Γ paths, the double nodal-line evidence can be verified by seeing the zoom-in views of the surface state.

In addition, we calculate the band structure of bulk W2O3I4 in the presence of SOC effect as shown in Fig. 2(d), in which the degenerate nodes are all gapped with 141, 33, 8, 150, 150, and 98 meV at the degenerate nodes along the Γ-C, Y-Γ, Γ-M, D-A, L-Γ, and Γ-V paths, respectively. Our first-principles calculations indicate that these opened nodes drive bulk W2O3I4 from a nodal-line semimetal to a topological insulator phase with a $Z_2$ number $= (0; 001)$, which means bulk W2O3I4 is a weak topological insulator. Its surface state by considering SOC is shown in Fig. S6(a) [41].

C. Electronic properties of monolayer W2O3I4

Similar to bulk W2O3I4, the band structure of monolayer W2O3I4 without the consideration of SOC effect and the partial density of state of each element are shown in Fig. S5(b) [41]. It is revealed that the conduction and valence bands near Fermi level are contributed by W $d$ and I $p$ orbitals. There are two degenerate nodes around the Fermi level along the Γ-0, D-Γ, and Γ-V paths, respectively. The orbital-resolved band structure is presented in Fig. 3(a) and it suggests that the nodal loop is induced by the band inversion between the conduction and valence bands without considering SOC effect. We calculate the band gap between the conduction and valence bands in the whole BZ and find that the degenerate nodes are connected to...
FIG. 3. (a) The orbital-resolved band structure of monolayer W\(_2\)O\(_3\)I\(_4\). (b) The band gap between the conduction and valence bands in the whole BZ. (c) The edge states near Fermi energy level of monolayer W\(_2\)O\(_3\)I\(_4\). (d) The band structure of monolayer W\(_2\)O\(_3\)I\(_4\) in the presence of SOC effect and the zoom-in views of the gap opening of degenerate nodes.

each other and form a closed nodal loop around the BZ center \(\Gamma\) point, as shown in Fig. 3(b).

As other 2D Dirac nodal lines reported before, an \(M_z\) mirror symmetry was required to ensure the gapless crossing of the in-plane nodal line. The configuration of monolayer W\(_2\)O\(_3\)I\(_4\) belongs to the \(Cmmm\) space group and contains the mirror plane \(M_z\), which protects the in-plane nodal line without SOC effect. Furthermore, we derived its topological edge state on its (100) boundary as shown in Fig. 3(c). Similar to the bulk state, we derived monolayer W\(_2\)O\(_3\)I\(_4\) band structure in the presence of SOC effect in Fig. 3(d) and it shows that the degenerate nodes are all gapped with 170 meV in \(\Gamma\)-\(A\), and 11 meV in \(D\)-\(\Gamma\), respectively. Our first-principles calculations indicate that SOC completely lifts the degeneracy of the nodal line and leads to a new state of \(Z_2\) number = 1, hence the monolayer W\(_2\)O\(_3\)I\(_4\) is a 2D topological insulator. Its edge state when considering SOC is shown in Fig. S6(b) [41]; we can clearly see there still exists the excitation of edge states in the path \(\Gamma\)-\(X\). The stacking of 2D topological insulator W\(_2\)O\(_3\)I\(_4\) with the weak van der Waals interlayer interactions makes the bulk W\(_2\)O\(_3\)I\(_4\) a weak topological insulator.

D. External field modulation of topological nodal lines in monolayer W\(_2\)O\(_3\)I\(_4\)

Strain engineering and external electric field are effective methods to regulate the properties of 2D materials [45,46]. We study the electronic structures of monolayer W\(_2\)O\(_3\)I\(_4\) under biaxial strain from \(-5\%\) to \(5\%\) and the calculated band structures are shown in Fig. 4. It turns out that the nodal line is

FIG. 4. The band structures of monolayer W\(_2\)O\(_3\)I\(_4\) under biaxial strain ranged from \(-5\%\) to \(5\%).
highly stable under biaxial strain in the absence of SOC effect, with only small change to the energy band near the Fermi level moving upward and downward. This can be understood by the fact that the monolayer W$_2$O$_3$I$_4$ is robust under biaxial strain and its vertical mirror symmetry is not broken under the biaxial strain. However, when we apply the out-of-plane external electric field of 0.01 eV/Å to check the calculated band structures as shown in Fig. S7 [41], the nodal line is destroyed because of the vertical mirror symmetry breaking under electric field. The applied out-of-plane electric field makes all degenerate nodes gapped and the monolayer W$_2$O$_3$I$_4$ turns into the topological insulators even in the absence of SOC effect. The tunability of the nodal line under biaxial strain and electric field in the absence of SOC effect implies that the monolayer W$_2$O$_3$I$_4$ may have potential applications in nanoelectronic devices.

III. COMPUTATIONAL METHODS

First-principles calculations were performed by using the Vienna *ab initio* simulation package (VASP) [47]. The exchange-correlation potential was treated by the generalized gradient approximation of the Perdew-Burke-Ernzerhof (PBE) type [48]. In the calculations for optimization of bulk and monolayer W$_2$O$_3$I$_4$, the DFT-D3 correction method is used to obtain a more accurate description of the interlayer van der Waals interaction [49]. The cutoff energy for plane-wave expansion was 600 eV for both monolayer and bulk W$_2$O$_3$I$_4$. The k-point sampling grids in the self-consistent calculations are $4 \times 4 \times 1$ and $4 \times 4 \times 3$ for monolayer and bulk W$_2$O$_3$I$_4$, respectively. The crystal structure was fully relaxed until the residual forces on each atom became less than 0.0001 eV/Å and the energy precision became less than $10^{-8}$ eV. A vacuum of 20 Å between layers was used to model the monolayer W$_2$O$_3$I$_4$. The Wannier-based Hamiltonian was constructed by using the WANNIER90 package [50]. The comparisons of band structure for bulk W$_2$O$_3$I$_4$ and monolayer W$_2$O$_3$I$_4$ were calculated by using PBE and WANNIER90 methods as shown in Fig. S8 [41]. We can find they match each other very well around the Fermi level, so that the Wannier-based Hamiltonian is trustworthy for studying the topological properties here. The gap between $N_{occ}$ and $N_{occ+1}$ bands in the whole BZ, all nodes

IV. CONCLUSIONS

In summary, we investigate the electronic structures and lattice dynamics of bulk and monolayer W$_2$O$_3$I$_4$ by means of first-principles calculations. Our results reveal that both W$_2$O$_3$I$_4$ bulk and monolayer are nodal-line semimetals in the absence of SOC effect; the occurrence of their nodal lines is mainly due to the band inversion between conduction and valence bands. Moreover, W$_2$O$_3$I$_4$ bulk and monolayer exhibit excellent thermal stability and the nodal line in monolayer W$_2$O$_3$I$_4$ is located around the $\Gamma$ point and there are two closed nodal loops in bulk W$_2$O$_3$I$_4$ in the absence of SOC effect. Furthermore, we study the external field modulation of topological nodal lines in monolayer W$_2$O$_3$I$_4$ without SOC effect which is quite robust under biaxial strain, and the nodal line is destroyed by the vertical mirror symmetry breaking under an external electric field. Finally, the W$_2$O$_3$I$_4$ should open up a band gap when the SOC effect is considered, and both its bulk and monolayer become topological insulators.

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