Square transition-metal carbides MC$_6$ (M = Mo, W) as stable two-dimensional Dirac cone materials

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Searching for new two-dimensional (2D) Dirac cone materials has been popular since the exfoliation of graphene. Herein, based on density functional theory, we predict a novel family of 2D Dirac cone materials in square transition-metal carbides MC$_6$ (M = Mo, W) which show inherent stability confirmed by phonon spectrum analysis and ab initio molecular dynamics calculations. The Dirac point, located exactly at the Fermi level, mainly arises from the hybridization of M-$d_{z^2}$ and C-$p_z$ orbitals which gives rise to an ultra-high Fermi velocity comparable to that of graphene. Moreover, strong spin–orbit coupling related to M-$d$ electrons can generate large band gaps of 35 and 89 meV for MoC$_6$ and WC$_6$ monolayers, respectively, which allows MC$_6$ materials to be operable at room temperature (26 meV), as candidates for nanoelectronics in the upcoming post-silicon era. The conceived novel stable metal–carbon framework materials provide a platform for designing 2D Dirac cone materials.

Introductions

Since the experimental observation of monolayer graphene,$^1$ two-dimensional (2D) Dirac cone materials, characterized by linear band dispersion at the Fermi level, have attracted intense attention due to their unique physical properties and potential applications in nanoscale devices.$^2,^3$ In particular, the Dirac fermions in graphene give rise to an ultra-high carrier mobility$^4,^5$ and half-integer/fractional/fractal quantum Hall effects$^6,^7$ which offer a broad perspective for the development of dissipationless applications.$^8$ Meanwhile, previous reports have theoretically realized the quantum anomalous Hall effect by proximity coupling graphene to an antiferromagnetic insulator (BiFeO$_3$).$^1^1$ These exotic behaviors in graphene have motivated the continuous search for novel 2D Dirac materials.$^{12}$ This has yielded a crowd of 2D carbon allotropes discovered experimentally or theoretically, including graphene (e.g. x, x2-, β, δ, 6,6,12-, 4,12,2- and 4,12,4-graphyne)$^{13–16}$ ph-graphene,$^{17}$ x-graphene (x = S, D, and E)$^{18}$ and phagraphene,$^{19}$ which also show linearly dispersed band structures with intrinsic massless fermions. Meanwhile, some other 2D systems, such as silicene,$^{20}$ germanene,$^{20}$ stanene allotropes,$^{21–23}$ boron allotropes,$^{24}$ organometallic crystals,$^{25,26}$ and transition metal compounds,$^{27–30}$ have been verified to be Dirac cone materials.

Among the abundant candidates, 2D transition metal materials stand out from the competition due to their strong spin–orbit coupling (SOC) effects which usually open up large band gaps suitable for realistic applications in the next generation of faster and smaller field-effect transistors.$^{27–30}$ Considering the importance of carbon in modern device applications, transition metal carbides are a long sought goal. MXenes,$^{31}$ one kind of 2D transition-metal–carbon material, have already been synthesized experimentally and possess potential applications in supercapacitor electrodes,$^{32}$ energy storage,$^{33}$ metal ion batteries$^{14}$ and superconducting crystals.$^{35}$ In the meantime, theoretical computations have revealed several generations of 2D transition metal–carbon materials to be intrinsic topological insulators (TIs) including triangular MXenes with d-band topological order,$^{36,37}$ hexagonal organometallic TIs with benzene molecular building blocks$^{25,26}$ and rectangular transition metal carbides with quasiplanar tetracoordinate C atoms.$^{29,30}$ These results greatly enrich the physics of 2D transition metal carbides and pave new ways for designing C-based materials for realistic applications. However, rare Dirac materials have been found in transition metal–carbon compounds and only a few rectangular 2D phases$^{29}$ and organometallic lattices$^{25,26,38}$ have been reported without experimental synthesis. Therefore, exploring new 2D Dirac cone materials in C-based transition metal compounds with sizable band gaps is still a priority to guide efforts in experiment and theory.

In this work, we have designed a novel family of 2D materials of square transition-metal carbides MC$_6$ (M = Mo, W) which are zero-gap semimetals with Dirac cones at off-symmetry reciprocal sites in the absence of SOC. We demonstrated that the distinct Dirac cones at the Fermi level are mainly derived from...
M-d_{x^2-y^2},d_{3z^2-r^2} and C-p_z orbitals. The SOC effects open large band gaps of 35 and 89 meV for MoC_6 and WC_6, respectively. Our predicted square transition metal–carbon monolayers with high Fermi velocity could provide a new choice for realizing Dirac materials beyond hexagonal lattice symmetry.

Methods

First-principles calculations were performed within the framework of the Perdew–Burke–Ernzerhof (PBE) generalized gradient approximation (GGA), as implemented in the Vienna ab initio simulation package (VASP). The property calculations were performed with plane-wave basis sets of 500 eV on the 11 × 11 × 1 Monkhorst–Pack k-point mesh. A slab model with a vacuum layer larger than 15 Å was employed and all geometry structures were fully relaxed until the residual forces on each atom were less than 0.01 eV Å⁻¹. The dynamic stabilities of the systems were checked by phonon calculations via the force-constant method, as implemented in the PHONOPY code. Thermal stability was also examined with ab initio molecular dynamics (AIMD) using the Nosé algorithm in the NVT ensemble at high temperature. Based on the projected densities of states (PDOS) calculated within density functional theory (DFT), we have constructed the tight-binding Hamiltonian on the basis of the maximally localized Wannier functions (MLWFs) and then computed the topological Z₂ invariant by tracing the Wannier charge centers using the non-Abelian Berry connection, as provided by the software package WannierTools.

Results and discussion

The novel 2D transition-metal carbides MC_6 (M = Mo, W) crystallize in the tetragonal space group P4/mmbm (no. 127) with a = b = 8.546–8.540 Å from Mo to W (Table 1). As shown in Fig. 1, the MC_6 monolayers are triple atomic layer structures with Mo/W atomic layers sandwiched between two C atomic layers. All of the transition-metal atoms are coordinated in a slightly distorted [MC_6] octahedron with the six nearest neighboring C atoms for MC_6 monolayers. There are one independent M atom (M, site symmetry 4h) and two crystallographically unique C atoms (C1, site symmetry 16i; C2, site symmetry 8k) with a chemical formula of MC_6 in one unit. In order to distinguish our structures from the reported hexagonal MC_6 (M = Mo, W), we denote square MC_6 as s-MC_6 and hexagonal MC_6 as h-MC_6 (Fig. S1, ESI†). The length of the C–C bonds in s-MC_6 range from 1.410 to 1.420 Å. These results, analogous to those of h-MC_6 (1.410 Å), are quite in accordance with the length of C–C bonds (1.420 Å) in graphene. The similar values of the C–C bond length indicate sp² hybridization between three adjacent C atoms that favors a strong extended π bond. The length of the M–C bonds is calculated to be 2.068–2.129 Å and 2.084–2.113 Å for s-MoC_6 and s-WC_6 monolayers, respectively. These results are close to those in h-MC_6 and TM_2CO_2 (M = Mo, W), in which the transition-metal atoms bonding with C atoms have been proven to be stable.

To evaluate the stability of the hypothetical structures, we first computed the formation energy with respect to the bulk metals and graphene, defined as below:

\[ E_f = \frac{E_{2D} - n_M E_M - n_C E_C}{n_M + n_C} \]

where \( E_{2D} \) is the total energy of the monolayers, and \( E_M \) and \( E_C \) are the energies of bulk M metals and graphene per atom, respectively. Our results show that s-MoC_6 and s-WC_6 monolayers have formation energies of 1.38 and 1.33 eV per atom, respectively, which are slightly larger than those of h-MoC_6 (1.30 eV per atom) and h-WC_6 (1.25 eV per atom) monolayers. The very similar formation energies suggest that s-MC_6 and h-MC_6 monolayers are equally stable. The positive values mean that the experimental synthesis of MC_6 monolayers is an endothermic process and can be achieved by epitaxial growth on an appropriate semiconductor surface.

The phonon spectrum and projected phonon density of states (PDOS), shown in Fig. 1b and c, are calculated to focus on the examination of the dynamic stability for the s-MC_6 monolayers. All of the branches over the entire Brillouin zone are appreciably positive phonon vibration modes, establishing that the s-MC_6 monolayers are at local minimums of energy. From the PDOS, it can be seen that the phonon mode mainly contains the M atom vibrations in the low-energy region.
In-plane axial Young’s modulus, defined as  are mechanically stable square lattices. Correspondingly, the contributions mainly stem from strong p-conjugated bonds. Notably, the highest frequencies in the phonon spectra of the s-MoC₆ and s-WC₆ sheets can reach up to 46.42 and 46.62 THz, respectively, which are slightly less than those in h-MC₆ (Mo, 47.08 THz; W, 47.33 THz), indicating almost a similar stability for the square and hexagonal structures. Compared to the conventional sandwich structures of transition metal compounds, the values of the highest phonon vibration in the s-MC₆ monolayers are obviously greater than those in h-MoN₂ (20–25 THz) and MoS₂ (13.25–13.85) monolayers.

Additionally, we checked the mechanical stability of s-MC₆ monolayers by calculating the linear elastic constants. The 2D linear elastic constants in units of N m⁻¹ are calculated to be $C_{11} = 84.38$, $C_{12} = 69.57$ and $C_{44} = 34.44$ for the s-MoC₆ monolayer, and $C_{11} = 91.12$, $C_{12} = 73.88$ and $C_{44} = 38.18$ for the s-WC₆ monolayer. For the square lattice, the Born criteria for structural stability is defined as follows:

$$C_{11} > |C_{12}|, C_{44} > 0$$

It is obvious that the elastic constants of s-MC₆ monolayers fulfil the condition of the Born criteria. So, the s-MC₆ sheets are mechanically stable square lattices. Correspondingly, the in-plane axial Young’s modulus, defined as $E = (C_{11} - C_{12}^2)/C_{11}$, is calculated to be 27.02 and 31.22 N m⁻¹ for s-MoC₆ and s-WC₆, respectively, which are much lower than that of graphene (340 N m⁻¹), penta-graphene (263.8 N m⁻¹) and the MoS₂ monolayer (123 N m⁻¹). Such values indicate the relatively good elastic properties and demonstrate the feasibility of s-MC₆ monolayers being rolled into nanotubes.

Finally, we examine the thermal stability of the s-MC₆ monolayers by carrying out AIMD simulations (Fig. S2, ESI†). After heating for 5 ps at a temperature of 500 K, the s-MC₆ structures do not suffer drastic structural distortion or transformation and can be optimized back to the initial structures through a relaxation calculation. However, the snapshots of the s-MC₆ monolayers at 1000 K show a serious distortion of the geometry. The total potential energies of the s-MC₆ monolayers only fluctuate around a certain constant magnitude for AIMD running at 500 K (Fig. S3, ESI†). Therefore, it can be concluded that both of the estimated melting temperatures of the two monolayers are between 500 and 1000 K.

To study the electronic properties of the s-MC₆ monolayers, we calculated the orbital-resolved band structures and depict them in Fig. 2. The monolayers are zero-band-gap semimetals with the valence band (VB) and conduction band (CB) touching each other at off-symmetry points of [0.21, 0.21] and [0.20, 0.20] from the R to the Γ point for s-MoC₆ and s-WC₆, respectively, in the absence of SOC (Fig. 2a and b). It can be seen that the linear band dispersion appears in the range of −0.1 to 0.2 eV, which causes Dirac cones around the Fermi level. The three-dimensional (3D) plot for the Dirac cones is illustrated in Fig. 3, which presents a notable circular-cone character around the Fermi level. As shown in Fig. S4 (ESI†), the Dirac band structures of the s-MC₆ monolayers were checked at the GGA+U level with $U = 2.81$ eV, $J = 0.59$ eV ($U = 2.67$ eV, $J = 0.54$ eV), and this was carried out in order to consider the Coulomb interaction effect for the Mo (W) atom, for which the Hubbard $U$ values have been tested and used in previous theoretical results. The Fermi velocity ($v_F$) values can be evaluated via the slope of the bands by the expression $v_F = \frac{\partial E}{\partial k}$.

$$v_F = 2.84 \times 10^5 \text{ m s}^{-1}, 3.23 \times 10^5 \text{ m s}^{-1}$$

and less than those of B-based 2D materials including borophane (3.0 × 10⁶ m s⁻¹), silicene (5.31 × 10⁵ m s⁻¹), and more than those of graphene (8.22 × 10⁵ m s⁻¹) and silicene (5.31 × 10⁵ m s⁻¹). To benchmark our computational results, the Fermi velocity, calculated for graphene at the same theoretical level, is 8.43 × 10⁵ m s⁻¹ and 8.42 × 10⁵ m s⁻¹ along the line perpendicular to the Γ-K direction, which is in good agreement with the previous results.
When taking into account the SOC effect, the Dirac band structure is well retained except for an enlarged band gap of 35 meV at the Dirac point for the s-MoC$_6$ monolayer (Fig. 2c). In the case of the s-WC$_6$ monolayer, the degenerate states at the touching point are lifted out with an energy gap of 89 meV, which provides the band structures around the Fermi level from the linear crossed bands to the quadratic bands. The band gaps, recalculated at the GGA+U level with SOC, are 37 meV and 87 meV for the s-MoC$_6$ and s-WC$_6$ monolayers, respectively (Fig. S4, ESI†). These values are much larger than those of graphene, silicene, and germanene which have small gaps in the order of meV. For both of the s-MoC$_6$ and s-WC$_6$ monolayers in the vicinity of the Fermi level, the valence band maximum (VBM) and conduction band minimum (CBM) are mainly originated from the Mo-$d_{z^2}$, Mo-$p_z$, and C-$p_z$ orbitals as well as having indispensible contributions from the C-$p_z$ orbital by the projection analysis.

In order to gain more insight into the Dirac behavior of the s-MC$_6$ sheets, the electron localization function (ELF) and the partial charge densities at the Dirac points were calculated (Fig. 4). The ELF for s-MoC$_6$ shows that there are high electron localization regions between two adjacent carbon atoms, indicating obvious p electrons in carbon rings in analogy to the h-MC$_6$ monolayers. In the real space, the partial charge densities of the CBM (Fig. 4c) and VBM (Fig. 4d) clearly confirm that the cooperation of the Mo-$d_{z^2}$, Mo-$p_z$, and C-$p_z$ orbitals is responsible for the formation of the Dirac cones. The same characteristics also appear in the square s-MoS$_2$ monolayer, in which the four pear-shaped lobes of the in-plane Mo-$d_{z^2}$-$p_z$ orbitals are compatible with the square lattice symmetry which leads to the formation of the Dirac cones. This is different from conventional graphite which does not easily achieve Dirac fermions in a square lattice with full symmetry.

It should be mentioned that previous studies have revealed an intrinsic quantum spin Hall (QSH) insulating feature in graphene, silicene, germanene, and stanene allotropes with Dirac states. With respect to the s-MC$_6$ monolayers with inversion symmetry in the structures, we also checked whether such a non-trivial topological state exists in the sheets via calculation of the well-defined $Z_2$ topological invariant established using the scheme proposed by Fu and Kane. Herein, the topological invariant $Z_2 = 1$ characterizes a non-trivial topological phase, while $Z_2 = 0$ indicates a trivial topological phase. The detailed parities of the occupied bands for the s-MC$_6$ monolayers are listed in Fig. S3 (ESI†). Our computational results yield a trivial topological invariant $Z_2 = 0$, indicating that the monolayers are just trivial nanostructures without the presence of the QSH effect. The results have also been verified by the analysis of helical gapless edge states using the WannierTools code (Fig. S6, ESI†), which is different from other QSH insulators.

To examine the stability and robustness of the Dirac cones for device applications, external biaxial strain was applied to the s-MC$_6$ monolayers by changing the lattices as $a = (a - \Delta a)/a_0$, where $a_0$ is the strained (equilibrium) lattice constant. It is found that the Dirac cones are robust to strain and can be well preserved within the strain range of $-10\%$ to $7\%$ and $-10\%$ to $9\%$ for the s-MoC$_6$ and s-WC$_6$ monolayers, respectively (Fig. 5). For the s-MoC$_6$ monolayer, when the stretching strain is increased up to $6\%$, the Dirac cones are slightly tilted at the boundary between electron and hole pockets. With the stretching strain increasing over $8\%$, the Dirac cones disappear with the parabolic VB and CB touching at the $\Gamma$ point in the absence of SOC. Although applying SOC can open up the gaps at the $\Gamma$ point, the Fermi level still passes through the conduction band, leading s-MoC$_6$ into a metal phase (Fig. S7, ESI†). For the s-WC$_6$ sheet, there is always a band gap in a large strain range from $-10\%$ to $10\%$ (Fig. S7, ESI†). When the stretching strain reaches up to $8\%$, strongly tilted Dirac cones emerge with a new type of Dirac fermion named type-II Dirac fermions, in contrast to the type-I Dirac fermions in graphene. When applying a stretching strain up to $10\%$, the VB and CB touch
at the $I$ point and the Dirac cones vanish at off-symmetry reciprocal sites (Fig. 5b). Such robust topology against external biaxial strain makes s-MC$_6$ easier for experimental realization and characterization.

Experimentally, high-quality graphene$^{58}$ and MoS$_2$,$^{73}$ have been successfully grown on substrates in their intrinsic strain limit ($\sim$15% for graphene and $\sim$11% for MoS$_2$) without substantially damaging their crystal structures. Thus, it is expected that the s-MC$_6$ monolayers can also be fabricated or transferred on the substrate. SiO$_2$, as a common large-gap insulator, has been successfully used as the substrate to grow high-quality polycrystalline MoS$_2$ monolayers or organic molecules.$^{74,75}$ Therefore, we selected T-silica (3 × 3: 8.387 Å)$^{76,77}$ as the substrate to support the s-MoC$_6$ monolayer as an example. To correctly describe the van der Waals interaction, a reliably dispersion-corrected DFT method (DFT-D2) has been used.$^{78}$ The optimized distance ($d$) between adjacent layers was found to be 3.037 Å. Fig. S8 (ESI†) displays the optimized crystal structure and calculated band structure for the MoC$_6@$SiO$_2$ film with intrinsic Dirac cones, which demonstrates the robustness of the Dirac structures.

Conclusions

In summary, we predict s-MC$_6$ (M = Mo, W) as a new family of 2D materials with intrinsic Dirac states based on first-principles calculations. The hybridization of M-d$_{z^2}$ and C-p$_{z}$ bands endows sheets with an ultrahigh Fermi velocity comparable to that of graphene. Owing to the strong SOC of transition metal atoms (Mo and W), sizable band gaps of the s-MC$_6$ monolayers are calculated to be 35 and 89 meV for MoC$_6$ and s-WC$_6$, respectively. Our results demonstrate that the Dirac states are robust against applied external biaxial strain. These interesting results would not only stimulate further efforts on transition metal carbides but also provide a new pathway to engineer 2D materials.

Conflicts of interest

There are no conflicts to declare.

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References

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